Understanding the Origin of Selectivity in the Asymmetric Lithiation Reaction of *N*-Heterocycles: A Theoretical Study

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Abstract

The natural abundance of the *N*-heterocycle containing compounds has pushed the synthetic community toward the invention of new synthetic methods that result in the structural diversity of *N*-heterocycles. Among this, is the efficient and highly selective diamine mediated asymmetric lithiation process. Amongst the diamine chiral ligands, (-)-sparterine, which is a naturally occurring alkaloid proved to be an efficient one. Many successful, good yielding and highly selective lithiation reactions have been accomplished with the mediation by this chiral diamine base. Although, there are some examples of experimental and theoretical mechanistic studies in the literature, there is a lack of detailed understanding as to how it exactly induces the chirality.

In this thesis is described a systematic investigation of how (-)-sparteine influences the stereoselectivity in the course of asymmetric lithiation reaction. This led us to the establishment of the function of A-ring's β-CH_2 effect and D-ring effect. Consequently, the importance of the A-ring and D-ring portions of (-)-sparteine in the stereoselectivity is unraveled. Another part of this thesis deals with the asymmetric lithiation of BF_3-activated *N,N*- dimethylaminoferrocene in the presence of (1*R*, 2*R*)-N_1,N_2-bis(3,3-dimethylbutyl)-N_1,N_2-dimethylcyclohexane-1,2-diamine (a (*R*,*R*)-TMCDA surrogate) with *i*-PrLi. Computational findings were in full accord with the experimental observations. Subsequently, the theoretically provided insights into the mechanism of the reaction were exploited in computational design of a new ligand. Unfortunately, the outcome of this design was not experimentally robust and an updated approach towards a successful design was explained.

Acknowledgements

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Last but not the least; I would like to thank my family: my parents and my sister for supporting me throughout my life.

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Abbreviations

B3LYP	Becke, 3-parameter, Lee-Yang-Parr functional
Boc	Butoxy carbonyl
Bu	Butyl
CIPE	Complex Induced Proximity Effect
DFT	Density Functional Theory
ECP	Effective Core Potantials
ee	Enantiomeric excess
equiv	Equivalents
er	Enantiomeric ratio
HF	Hartree-Fock
i-PrLi	Isopropyl lithium
MP2	Second order Møller–Plesset perturbation theory
MTBE	Methyl *tert*-Butyl Ether
NMR	Nuclear Magnetic Resonance
OTs	Tosylate
Ph	Phenyl
RDS	Rate-Determining Step
TES	Triethylsilyl
TIPS	Triisopropylsilyl
TMS	Trimethylsily
TMCDA	Tetramethylcyclohexyl diamine

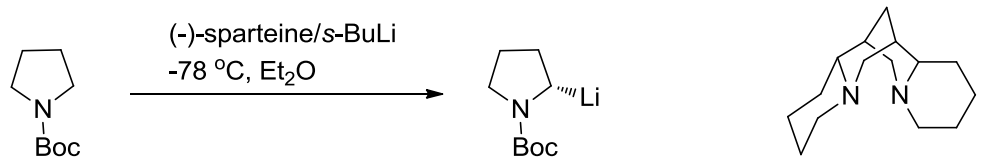
1. Introduction

The occurrence and biological importance of the *N*-containing heterocycles in many natural products as well as existing pharmaceuticals, has drawn the attention of the synthetic community toward the elaboration and decoration of these entities. In this vein, developing clean and efficient organic reactions to achieve this goal has been a focus of many groups. Moreover, the development of additional methods for constructing these scaffolds would enable the practitioners of the field to prepare potentially other useful compounds having therapeutical applications. In general, organolithium chemistry has been extensively exploited in organic synthesis since its first appearance at the beginning of the twentieth century.[1] The use of lithium metal and organic halides for the purpose of preparing organolithium reagents was reported by Ziegler, Wittig and Gilman.[2-4] The idea of using additives such as diamines (*e.g.* TMEDA) which was pursued after enhanced reactivities of organolithium compounds was observed in the presence of these agents.[5]

1.1. Stereoselctive Deprotonations

1.1.a. α- Carbanions to Nitrogen

The preparation and subsequent use of lithiocarbanions α to nitrogen first appeared in the literature in 1991.[6] In this work the enantioselective deprotonation of *N*-boc pyrrolidine **1** was carried out in Et_2O at -78 ºC in the presence of *s*-BuLi, (-)-sparteine (**Figure 1.1)**.



1 (-)-sparteine

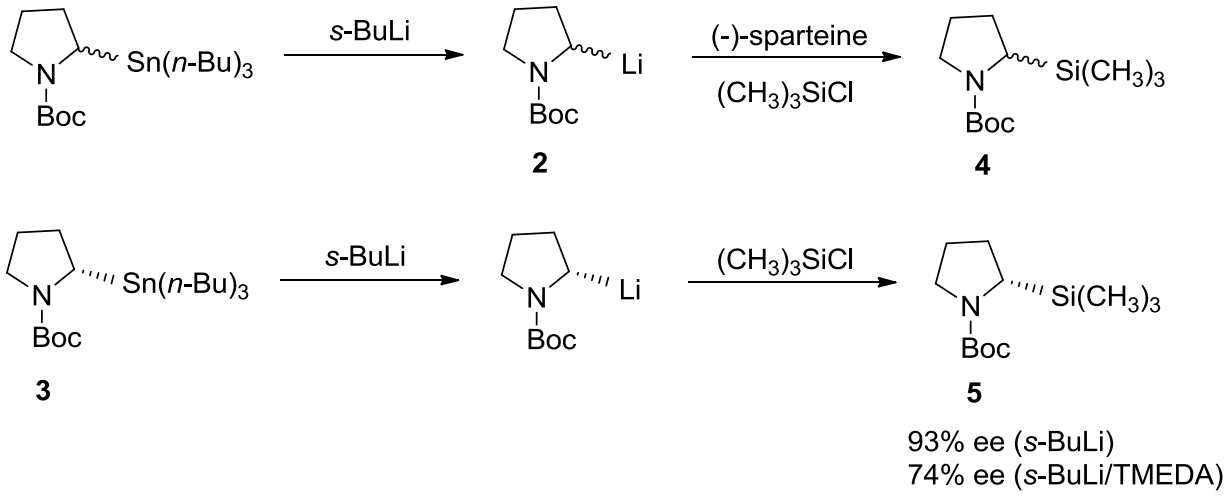
Figure 1.1. Asymmetric lithaition of *N*-boc pyrrolidine.

The reaction favoured the abstraction of *pro-(S)* hydrogen with a high level of selectivity (94% *ee*). In this same work the first steps towards understanding the mechanism and selectivity of this reaction were taken by the analysis of the transmetallation results. This is here that the enantioselectivity of the α-substitution reaction was attributed to the deprotonation step not the subsequent electrophilic quench. In 1992, Beak *et al*. reported the results of a work done to identify the main species involved in the lithiation process.[7] In this regard, they performed spectroscopic studies to investigate the *i*-PrLi/(-)-sparteine system in either Et_2O or cyclopentane or both to also clarify the potential role that solvent had on the reaction. The existence of the active complex as a dimer in Et_2O and as fluxional dimer species in hydrocarbon solvents was observed by NMR techniques. Interestingly, referring to their observations and several literature precedences[8-10], they concluded that the reaction proceeded through a dimer species, while not ruling out the possible intermediacy of monomeric species.

To determine where the selectivity occured in the lithiation-substitution process, Beak *et al*. conducted a more detailed study.[11] They did a series of deprotonation-substitution reactions on *N*-boc pyrrolidine **1** to establish the pathway by which the enantiomeric purity is reached. Based upon their findings two possible mechanisms were envisioned for this reaction. One possibility being the intermediacy of *s*-BuLi/(-)-

sparteine complex that produced a configurationally stable 2-lithiated intermediate which subsequently underwent substitution. The other plausible mechanism involved the formation of racemic 2-lithiated reagent that was enantioselectively transformed to the substituted product *via* (-)-sparteine asymmetric induction.

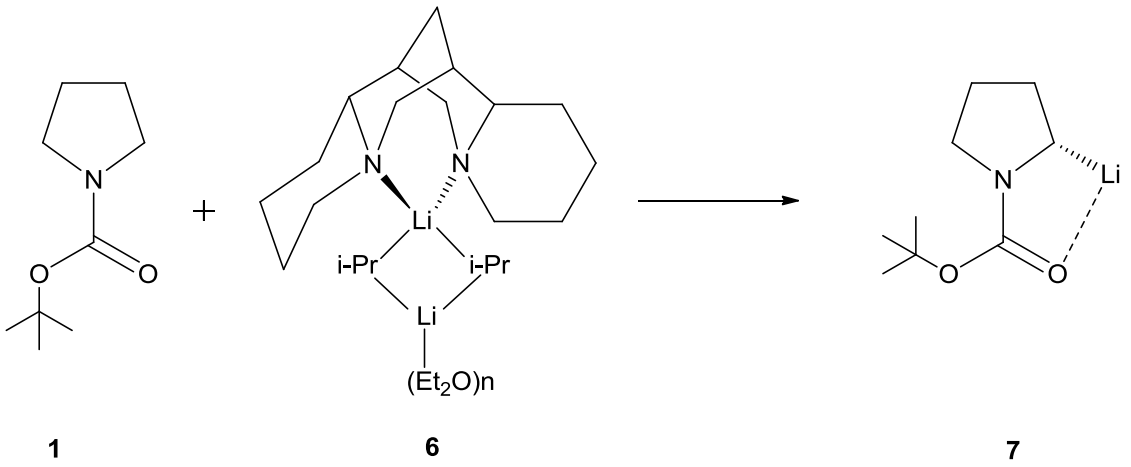
Given these findings the question remained whether the selectivity was associated with the first step or the second one. To address this question they set up two experiments to distinguish between the two hypotheses. First, the racemic 2-lithio-*N*-Boc pyrrolidine **2** was treated with TMSCl at -78 ºC followed by the addition of (-)-sparteine. The product **4** was found to be racemic. On the other hand, using the enantioenriched 2-lithio-*N*-Boc pyrrolidine and TMSCl, as the electrophile, furnished the 2-silylated product **5** in 93% *ee*. (**Scheme 1.1**). In addition, they carried out the reaction of (*S*)-2-(tris-*n*-butyltin)-*N*-Boc-pyrrolidine **3** with *s*-BuLi/TMEDA and obtained the same product with 74% *ee*. Furthermore, in this study they evaluated a set of lithiation-deuteration reactions to provide more evidence for the conclusion that deprotonation is the enantiodetermining step.



Scheme 1.1. Non-stereoselective versus stereoselective silylation of 2-(tris-*n*-butyl tin)-*N*-Boc pyrrolidine.[11]

In 1995, Beak and Gallagher reported their kinetic studies on the asymmetric deprotonation of *N*-Boc pyrrolidine done by the *i*-PrLi/(-)-sparteine system.[12] Their interest in investigating of base/diamine complexes arose from the fact that Hope *et al*. were successful in deprotonating carbamates using base/diamine combinations.[28]

In this work[12] they strove to determine the nature of the deprotonating complex and rate limiting step (RDS) of the reaction. Proton removal thought to occur by either complex **6** (**Scheme 1.2**) or alternatively a RLi/sparteine monomer formed from **6**. Later kinetic studies ruled out the involvement of either structure.



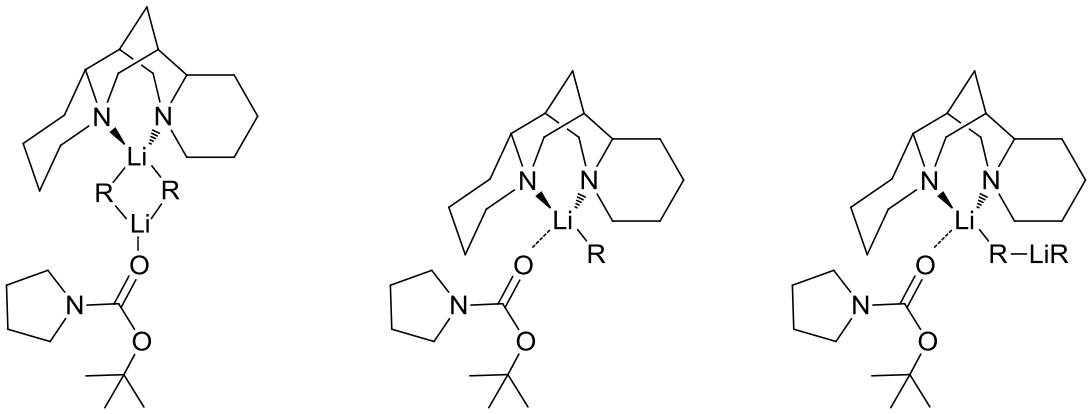
1 **6** **7**

Scheme 1.2. (-)-Sparteine mediated lithiation of *N*-Boc pyrrolidine.

Under the pseudo-first order experimental conditions, in the presence of excess **6**, reaction was found to be zero order with respect to the organolithium reagent. On the basis of these findings they proposed a scenario in which the formation of a *N*-Boc pyrrolidine/RLi/(-)sparteine prelithiation complex would take place. Further examination of their mechanism and related kinetic equations revealed the deprotonation step to be the RDS (Rate Determining Step) of the lithiation reaction. This was secured by the observation of a large intermolecular isotope effect (k_H/k_D=30) in the lithiation of a mixture of **2** and 2,2,5,5-tetradeutrio-*N*-Boc pyrrolidine. These results suggest the immediate formation of a prelithiation complex upon addition of substrate to the base-sparteine mixture. In this work, three possible structures for the prelithiation comlex were shown (**Figure 1.2**).

Complex **8** doesn't seem to be a suitable structure since (-)-sparteine is not in a proper position to induce chirality. The other two structures keep the substrate in a reasonable distance from the sparteine and make the asymmetric induction probable. In essence, reactions proceeding through either **9** or **10** should be considered. This concept

of complex induced proximity effect (CIPE) has been supported, by kinetic studies, for other cases such as amides and ureas as well.[13] However, the degree to which the CIPE is contributing to the reactions involving organolithium reagents, differ from case to case. The focus here, in the case of *N*-Boc pyrrolidine, is on the stereoselectivity of the deprotonation reaction and how efficiently the ligand (*i e.* sparteine) induces chirality. In this vein, the complexation and the way that reagents interact within the complex were of higher value to the investigator.



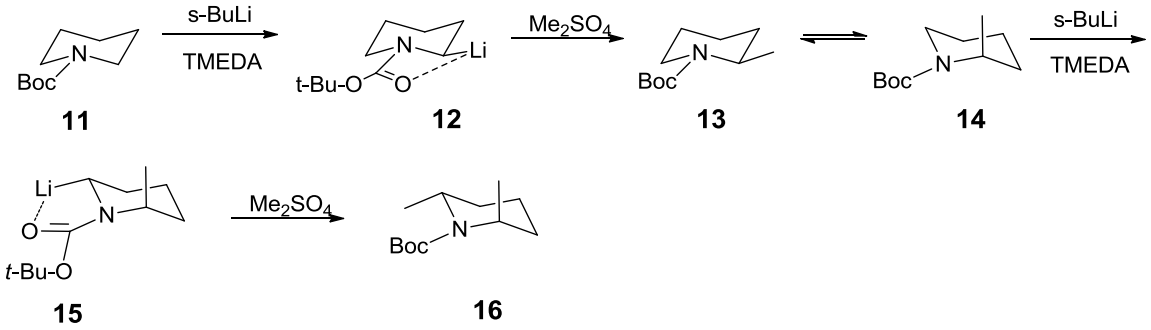
8 **9** **10**

Figure 1.2. Possible structures for the prelithiation complexes of **1** with (-)-sparteine.

In an account published in 1996, Beak *et al*. discussed in detail the reaction pathways leading to dipole stabilized carbanions, α to nitrogen, or benzylic carbanions, and their subsequent nucleophilic substitutions.[14] *N*-Boc piperidine **11** was used to demonstrate the regio- and diastereoselectivity of double lithiation-methylation reaction. It can be seen in Scheme 1.3 that the first lithiation places the Li in an equatorial position (**12**) (due to the more efficient interaction of carbonyl group and

lithium) followed by the first methylation (**13**). The equatorial 2-methyl substituent becomes axial (**14**) by a simple conformational interconversion in order to stabilize the system by relieving the **A**[1,3] strain.

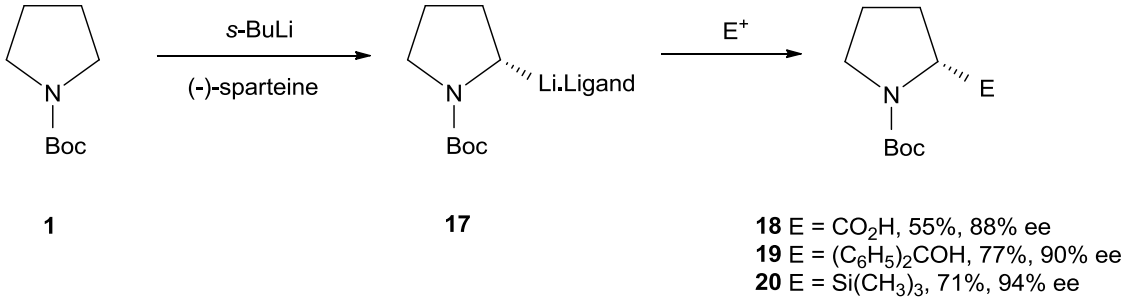
The regio- and diastereoselectivity in the second lithiation-methylation sequence leads to the intermediate **15** and the *anti*-2,6-dimethyl-*N*-Boc-pyrrolidine **16** (**Scheme 1.3**). The rationalizations for the observed selectivities were provided by reference to the theoretical studies done by Houk *et al*. in 1981.[15]



Scheme 1.3. Illustrative example of double lithiation-methylation reaction on *N*-Boc piperidine.

The discussion on when the enantioselection occurs has been brought up once more. The recognized role of (-)-sparteine in the asymmetric deprotonations was encouraging for Beak *et al.* to base their studies on the (-)-sparteine mediated asymmetric lithaition-substitutions.[16, 17]

N-Boc pyrrolidine **1** was treated with *s*-BuLi/sparteine followed by electrophilic quench by different electrophiles. Results are shown in scheme 4. Previously, the experiments by which the deprotonation was revealed to be the asymmetric step (enantio/diastereodetermining step), has been discussed. [6, 12]



Scheme 1.4. Asymmetric lithiation-substitution of *N*-Boc pyrrolidine.

To identify other possible chiral ligands that can be utilized in the asymmetric lithiation reaction, Beak *et al.* conducted another research.[18] In this work they prepared both enantiomers of each ligand in order to discover the structural features contributing to the chiral induction in the asymmetric lithiation-substitution of the *N*-Boc pyrrolidine. The research centered upon the synthesis and evaluation of the proline and bispidine chiral ligands. (-)-isosparteine, binaphthyldiamine and *trans*-cyclohexyl-1,2-diamine were also examined in this work. It was concluded that diproline-based diamino alcohol **21** and α-methylbenzylamine-derived bispidine **22**, **Figure 1.3**, were the most effective ligands.

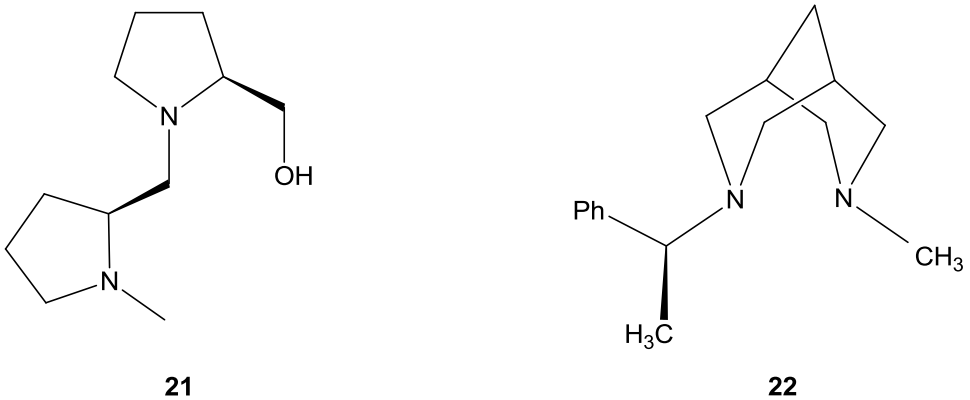
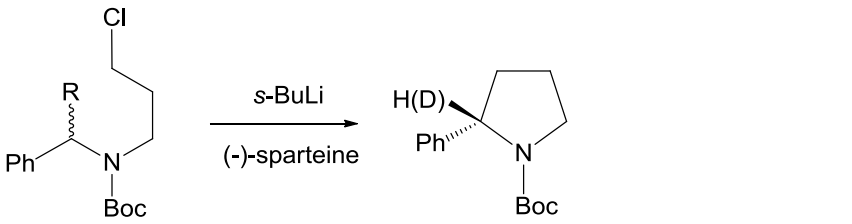


Figure 1.3. The most effective newly designed ligands for asymmetric lithiation.[18]

However, none of the ligands, studied in this work, had the effectiveness of (-)-sparteine in terms of conversion and enantioselection. It is simply explained that the proper ligand is the one that binds to the organolithium reagent in a balanced manner. Additionally, ligand should have the ability to expedite the lithiation reaction compared to a ligand-free reaction. Lastly, bringing the necessary steric interaction into the diastereomeric transition state as well as maintaining enough flexibility within the diastereomeric association required for the unification of the substrate, are other important qualifications needed for an efficient chiral ligand. To further investigate the operating mechanism in the successive lithiathion-substitution reactions, Beak *et al*. converted *N*-Boc-*N*-benzyl-3-chloropropylamine to (*S*)-*N*-Boc-2-phenylpyrrolidine **26**.[19]

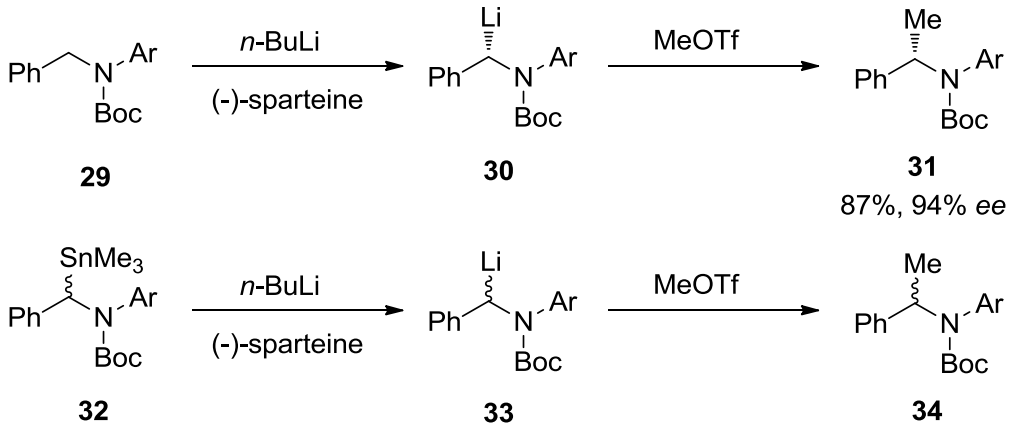


Scheme 1.5. Asymmetric lithiation-substitution on *N*-Boc-*N*-benzyl-3-chloropropylamine.[19]

Beak argues that indiscriminate deprotonation of racemic **24** would result in the preferential hydrogen removal which in turn gives a yield and *ee* comparable to that of non-deuterated substrate (**Scheme 1.5**). This behaviour was not observed in the reaction of **24.** In addition, tin-lithium exchange of racemic **25** gave a racemic product in the presence of (-)-sparteine. More in depth analysis of the reaction of **24** indicates that the

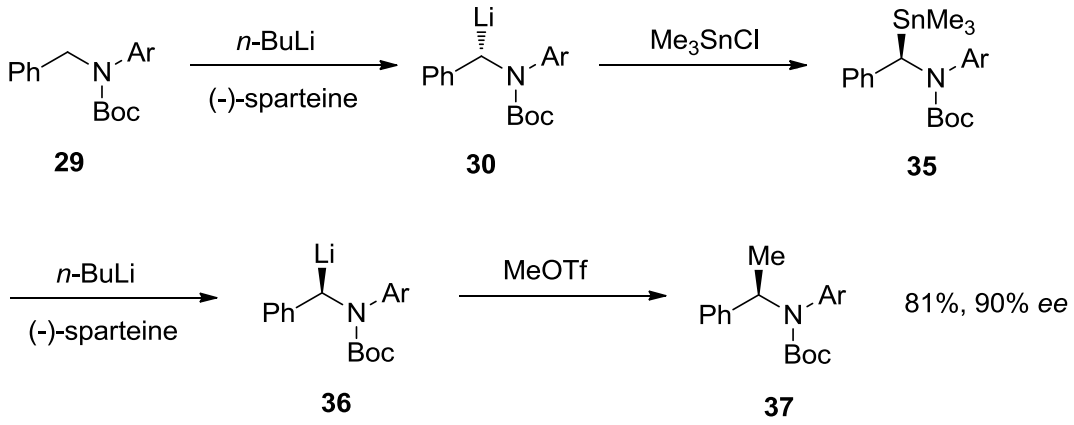
isotope effect overrides the enantioselectivity and that is the reason why the yield and *ee* for **2** differs from what has been observed for **23** (high kinetic isotope effects have been observed in other works).[20-22]

Other examples have also shown the involvement of an asymmetric deprotonation rather than an asymmetric substitution in the lithiation-substitution sequence. In 1996, Beak et al. used *N*-Boc-*N*-(*p*-methoxyphenyl) benzylamine (**Scheme 1.6**) as the substrate for the reaction.[23]



Scheme 1.6. Lithiation-methylation of *N*-Boc-*N*-(*p*-methoxyphenyl) benzylamine.[23]

It was shown that *n*-BuLi/Sparteine mediated deprotonation of **29** followed by substitution, furnishes the (*S*)-**31** with high stereoselectivity. The metal exchange of **32** with *n*-BuLi produces racemic lithiated product that results in the formation of racemic methylated product upon substitution with methyl triflate (**Scheme 1.6**).



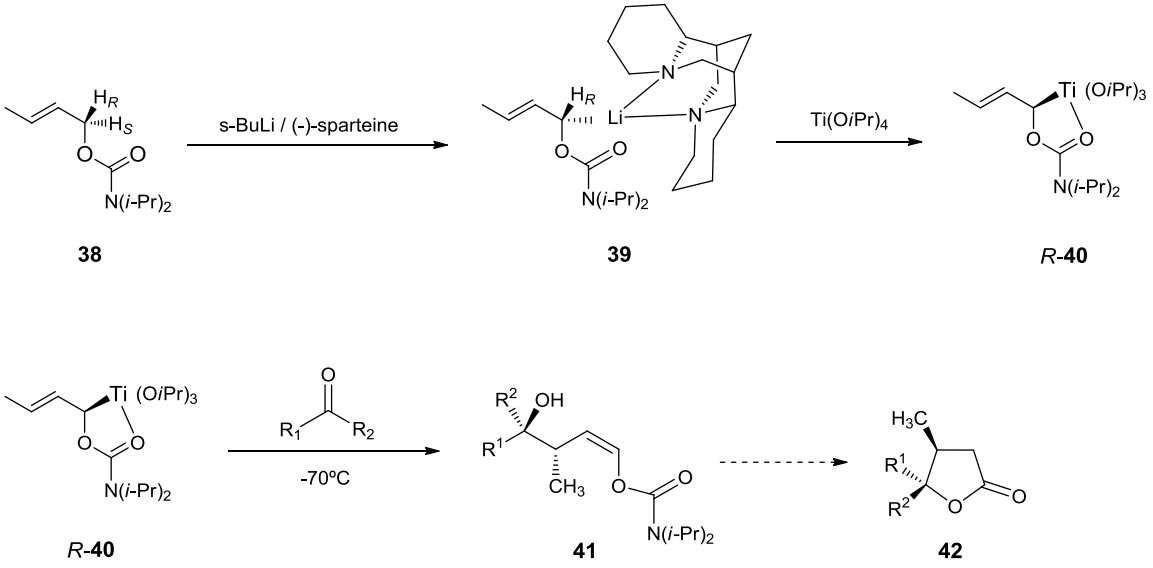
Scheme 1.7. Lithiation-methylation of *N*-Boc-*N*-(*p*-methoxyphenyl)benzylamine using two tin-lithium exchanges.[23]

Interestingly, the opposite enantiomer of **31** was prepared by a introducing a subtle change to the normal deprotonation-substitution sequence where two tin-lithium exchanges were done, the first of which was believed to invert the lithiated stereocenter leading to the inverted tin-substituted chiral center (**Scheme 1.7**). These results were supportive of the formation of configurationally stable lithiated intermediate.

1.1.b. α-Carbanions to Oxygen

The importance of the α-lithium compounds to oxygen in organic synthesis came to the focus as the configurationally stable aliphatic derivatives were discovered by Still et al.[24] In 1986, Hope *et al*. established the deprotonation of enantiomerically enriched secondary 2-alkenyl diisopropylcarbamates.[25] In another work they investigated the asymmetric deprotonation of 2-butenyl diisopropyl carbamate in the presence of (-)-sparteine and *s*-BuLi and used the carbanionic intermediate in the subsequent homoaldol reaction.[26, 27] This work comprises of a mechanistic and synthetic study by which the thermodynamically controlled asymmetric lithiation shows itself as the

governing factor in the reaction.[28] A detailed presentation of what has been done in this work is shown in **Scheme 1.8**.

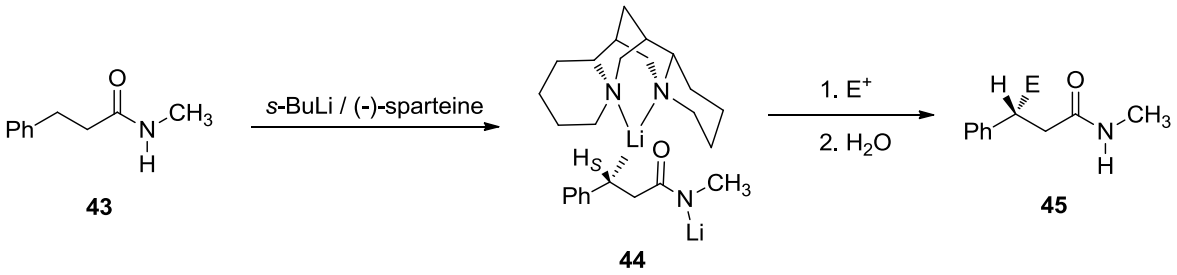


Scheme 1.8. Asymmetric lithiation, lithium-titanium exchange and enantioselective homoaldol reaction.[28]

In order to gain more insights into the structural features Boche *et al*. obtained the first crystal structure of η^1-[(1*S*,2*E*)-1-(*N*,*N*-diisopropylcarbamoyloxy)-3-trimethylsilyl-2-propene-1-yl]lithium**.**(-)-sparteine.[29] They observed (1*S*)-configuration of the lithiated center as well as the monomeric structure of the compound in the crystalline state. They also related the high selectivity of the carbonyl addition to the firm grasp of cation at the α-position. Furthermore, this rigidity can have contributions to the racemization barriers in chiral lithium derivatives.

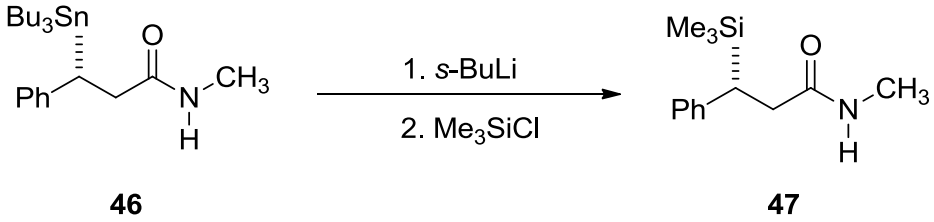
Benzyl carbamates were also subjected to the asymmetric lithiations.[30] This study shows the fairly ease of deprotonation with respect to the corresponding allyl esters. In addition, the relative stability of the lithiated intermediates was shown to be in favour of the secondary benzylcarbamates. *N*-Methyl-3-phenylpropionamide **43** was another

example of a primary benzyl carbamate lithiated with *s*-BuLi in the presence of sparteine. Lithiation and subsequent substitution with different electrophiles leads to substituted benzyl positions ranging from modest to high enantioselectivities (60-94%).[31,32] The introduction of (-)-sparteine after the deprotonation followed by the electrophilic quench gave the same results, suggesting the possible existence of equilibrating doubly-lithiated intermediates. This argument proved to be correct in another work by the same group.[33]



Scheme 1.9. Asymmetric lithiation with subsequent electrophilic quench of *N*-Methyl-3- phenylpropionamide **43** in the presence of (-)-sparteine.[31,32]

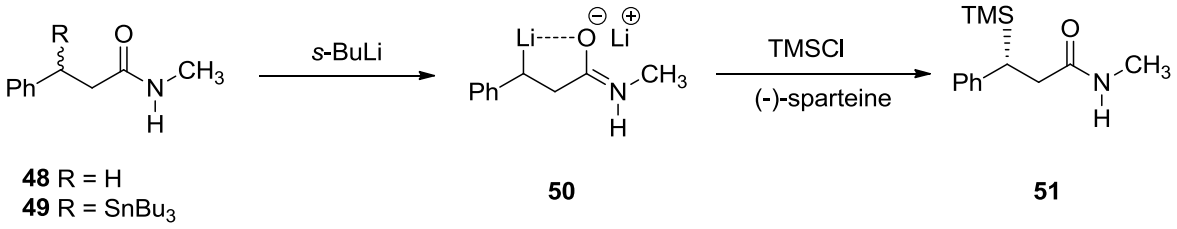
On the other hand, enantiomerically enriched stannane **46** was successfully silylated through a racemization-free lithiated intermediate (**Scheme 1.10**).[32]



Scheme 1.10. Transmetalation of stannane **46**.[32]

1.2. Asymmetric Substitution

In 1993, Beak *et al*. presented their observations on the asymmetric substitution instances they had with a number of electrophiles.[31] Reaction starts with the preparation of racemic lithiated agent **50** that undergoes an asymmetric substitution in the presence of (-)-sparteine. This gives **51** in 82% and 78% *ee* from **48** and **49** with 72% and 48% yields, respectively (**Scheme 1.11**).



48 R = H
49 R = $SnBu_3$

50

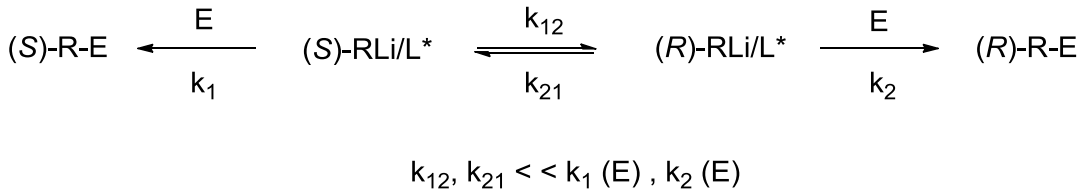
51

Scheme 1.11. Asymmetric substitutions of amide **48** and stannyl amide **49**.[31]

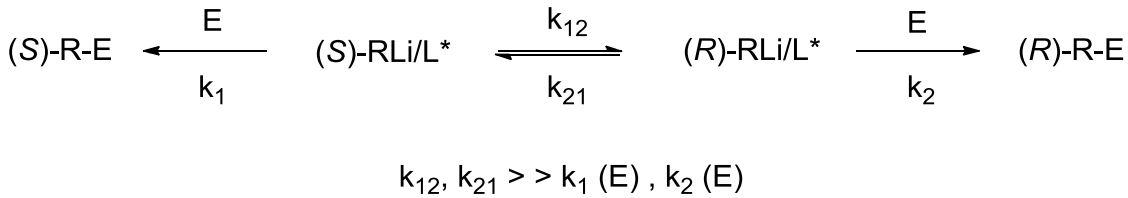
The use of racemic d_1 of **48** produces **51** with high *ee* and deuterium incorporation. These results rule out the possibility of involvement of asymmetric deprotonation in the sequence. In the light of various kinetic studies, [34-38] the proposition that the reaction can proceed through two possible pathways has been put together. This proposal makes the statement that the asymmetric substitution can proceed via *dynamic thermodynamic resolution* or *dynamic kinetic resolution*. As such, the enantioselectivity of the products is said to be determined by the *dynamic thermodynamic resolution* when the diastereomeric complexes between the organolithium and ligand are configurationally stable with respect to the rate of substitution. This way, the ratio of diastereomeric complexes verifies the final outcome of the reaction. On the other hand, the term *dynamic kinetic resolution* is used when the diastereomeric complexes are not stable

with respect to the rate of reaction with electrophile. As a result of this configurational lability, the enantioselectivity is dictated by the difference in the energy of the diastereomeric transition states for the reaction with electrophiles.

Equations 1.1 and 1.2 show the kinetic representations of these two possible pathways, respectively.



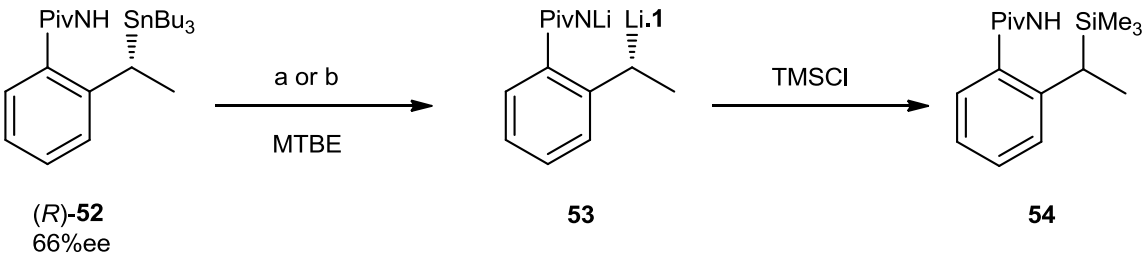
Equation (1.1) Kinetic expression for Dynamic Thermodynamic Resolution



Equation (1.2) Kinetic expression for Dynamic Kinetic Resolution.

To clearly illustrate the process of *Dynamic Thermodynamic Resolution*, the tin-lithium exchange of (*R*)- **52** with *s*-BuLi / (-)-sparteine and TMSCl was investigated by Beak et al. under two different conditions for lithiation.[38] As it is evident from Scheme 1.12, the warm-cool cycle produces (*R*)-**54** in 85% *ee*. On the contrary, the fixed temperature method gives rise to (*S*)-**54** with 62% *ee*. These results are in accordance with the pathway in which the diastereomeric complexes (**53**) reach an equilibrium state that is maintained after cooling to -78 ºC. This does not happen under the fixed

temperature conditions. In other words, the stereoinformation transfer is done with conformity where there is no warm-cool cycle involved.



(*R*)-**52**
66%ee

53

54

a) 1. *s*-BuLi/(-)-sparteine, -78 ºC (5 min)
2. -25 ºC (2h) 3. -78 ºC (30min)

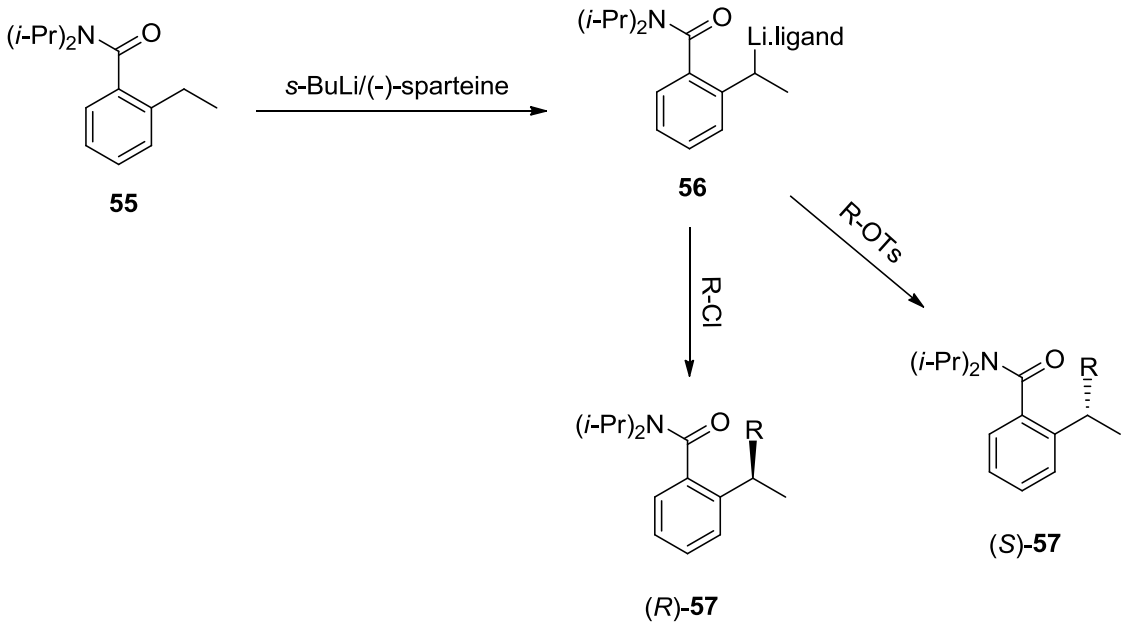
a. (*R*)-**54**, 85% ee

b) *s*-BuLi/(-)-sparteine, -78 ºC

b. (*S*)-**54**, 62% ee

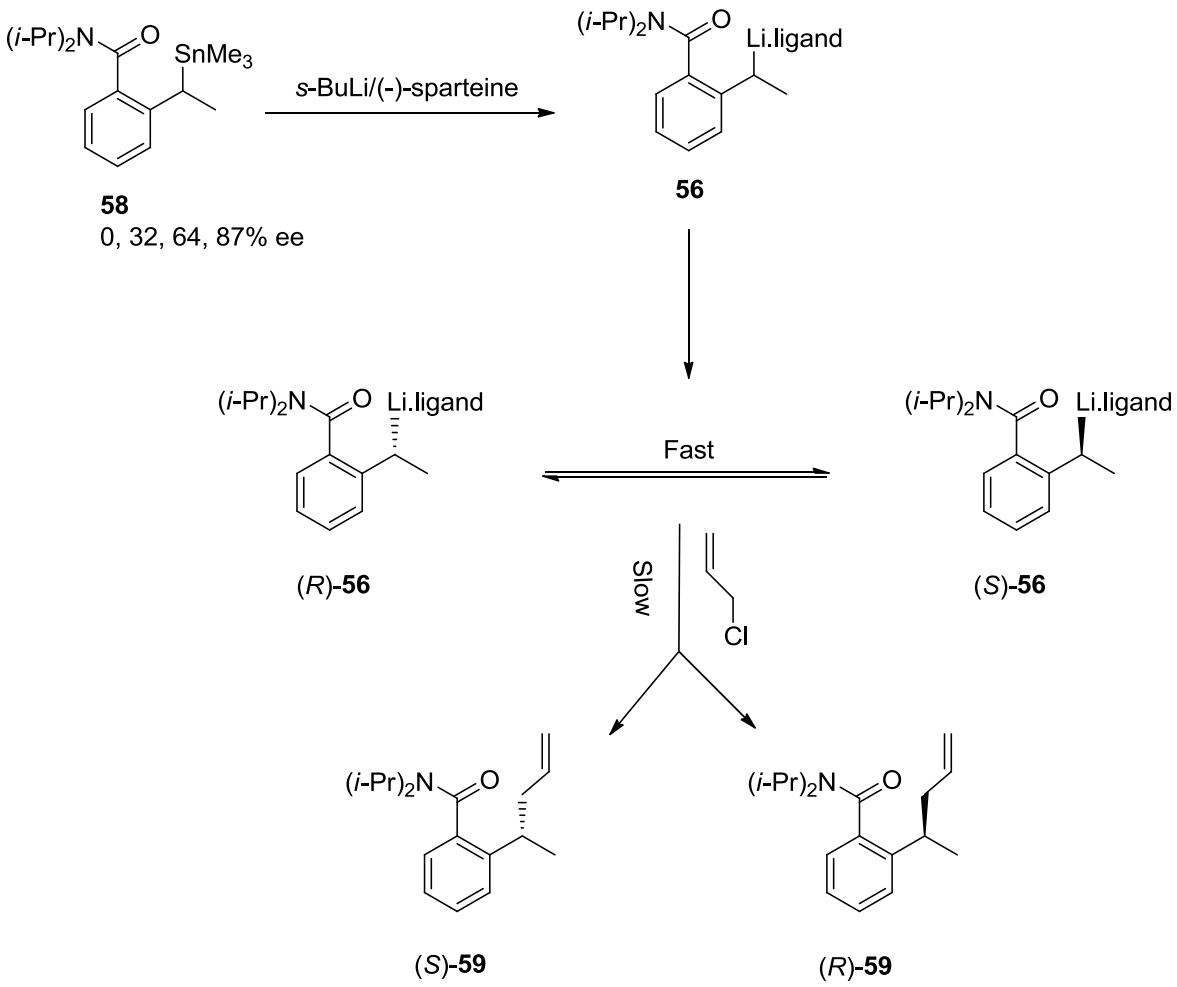
Scheme 1.12. Transfer of stereoinformation with fidelity or without, using different conditions.[38]

Another case of asymmetric substitution controlled by *Dynamic Kinetic Resolution* is shown in Scheme 1.13. lithiation of **55** with *s*-BuLi /(-)-sparteine produces the lithiated diastereomeric intermediate **56** which undergoes substitution in the presence of different electrophiles. The dependence of enantioselectivity on the nature of the electrophile, or to be more accurate, on the identity of nucleofuge, was clearly observed. For example, *n*-BuCl, *n*-BuBr, and *n*-BuI afforded the (*R*)- **57** with 80, 74 and 28% *ee*, respectively. The R-OTs electrophiles generated higher *ee* as opposed to the R-Cl reagents.[39]



Scheme 1.13. Asymmetric lithiation/substitution of **55**.[39]

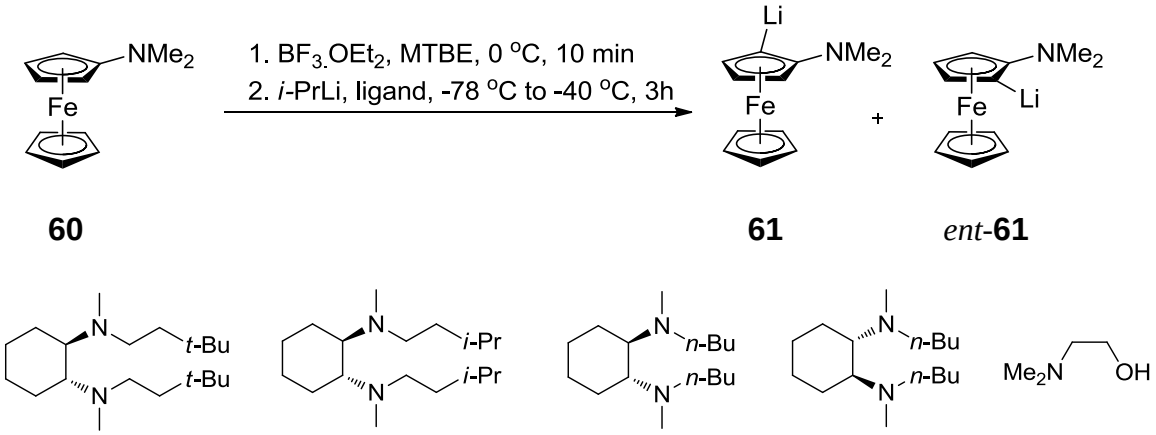
In another experiment, the treatment of organostannane **58** with *s*-BuLi /(-)-sparteine at -78 ºC followed by the addition of allylchloride forms (*R*)- **59** with 82-87% *ee* and independent of enantioenrichment of **58** (**Scheme 1.14**). It can be concluded that the diastereomeric lithiated complex is not configurationally stable. As such, the selectivity is determined by energy difference of involving diastereomeric transition states of the substitution step. This illustrates the *Dynamic Kinetic Resolution* pathway.



Scheme 1.14. Asymmetric lithiation/substitution of stannane **58**.

1.3. Asymmetric Lithiation of Aminoferrocenes

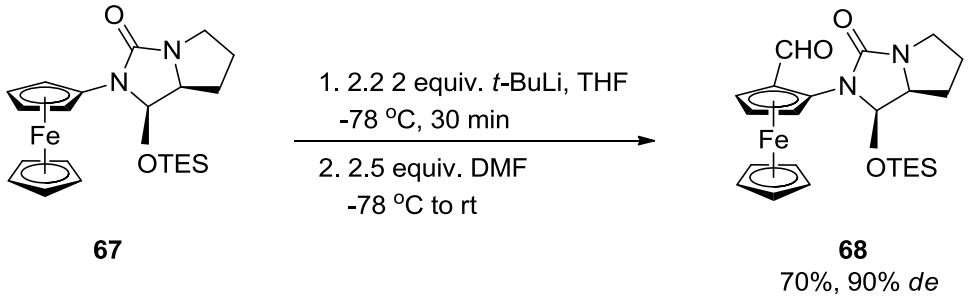
A majority of studies regarding the regioselective lithiation of activated tertiary amines focused on the lithiation of sp^3 hybridized carbon atoms. Kessar *et al*. showed in 2008 that BF_3-activated anilines undergo *ortho*- lithiation at -78 ºC. [40] At the same time, Metallinos *et al*. reported the lithiation of BF_3-activated dimethylaminoferrocene with *n*-BuLi in THF.[41] Their asymmetric lithiation method, tertiary aminoferrocenes are prochiral[24], produced different types of products in high yields (77-94%) after the electrophilic substitutions. Metallinos *et al*. also demonstrated, for the first time, that BF_3-activated tertiary aminoferrocenes undergo asymmetric lithiation with alkyllithiums in the presence of chiral 1,2-diaminocyclohexane-derived additives (**61**-**65**)[43].



Scheme 1.15. Asymmetric lithiation/substitution of BF_3-activated dimethylaminoferrocene.[43]

Testing the method with different organolithium compounds and chiral ligands revealed the effectiveness of the *i*-PrLi and (*R*,*R*)-**62** in producing the final mono-

substituted products in acceptable yields and enantiomeric excess. In 2012, Metallinos group also reported a diastereoslective synthesis of planar chiral ferrocenes using a proline-derivied chiral auxiliary. A lithiation/electrophilic quench protocol was used in this work to produce different planar chiral ferrocenes (**Scheme 1.16**).[43b]



67 **68**
70%, 90% *de*

Scheme 1.16. diastereoselective lithiation/substitution of *N*-susbstituted ferrocene **67**.[43b]

It should be noted that different non-amino based directing groups have been used by other researchers for the asymmetric lithiation of ferrocenes.[44, 45, 46] Furthermore, the asymmetric lithiation of isopropylferrocene done by Aratani, Gonda and Nozaki in 1970 is an example that illustrates the involvement of no directing group in the asymmetric lithiation of ferrocenes.[42]

1.4. Theoretical Studies with Regard to Asymmetric Lithiations of *N*-Heterocycles

Wiberg and Baily started computational studies on the asymmetric lithiation of *N*-Boc pyrrolidine in the presence of two different chiral ligands (-)-sparteine and (*S*,*S*)-1,2-bis(*N*,*N*-diethylamino)cyclohexane (*ent*-**62**) as well as two different organolithium bases.[47] Their calculations of the four most stable complexes showed the preferred

removal of the *pro*-(*S*) hydrogen of the Boc-protected pyrrolidine. A 3.2 kcal/mol difference in transition state free energies was in accord with the high experimental enantioselectivity of the lithiation of *N*-Boc pyrrolidine. The origin of selectivity said to arise from the short nonbonded distances within the diastereomeric transition states. Additionally, they compared the distance between the oxygen of the carbamate carbonyl group and the reacting hydrogen in their preferred transition state with the optimal distance of 2.78 Å reported by Beak[48] and found a close match. Other features of this work were the evaluation of the reaction in the presence of *t*-BuLi/(-)-sparteine and *i*-PrLi/ *ent*-**62**. It turned out that none of these combinations were as effective as the *i*-PrLi/(-)-sparteine mixture. In another work O'Brien, Wiberg, and Bailey performed a mixed experimental and computational study on the asymmetric lithiation of *N*-Boc pyrrolidine with *i*-PrLi and *s*-BuLi, mediated by sparteine-like chiral diamines.[49] The chiral inducing agents used in this study are depicted in Figure 1.4.

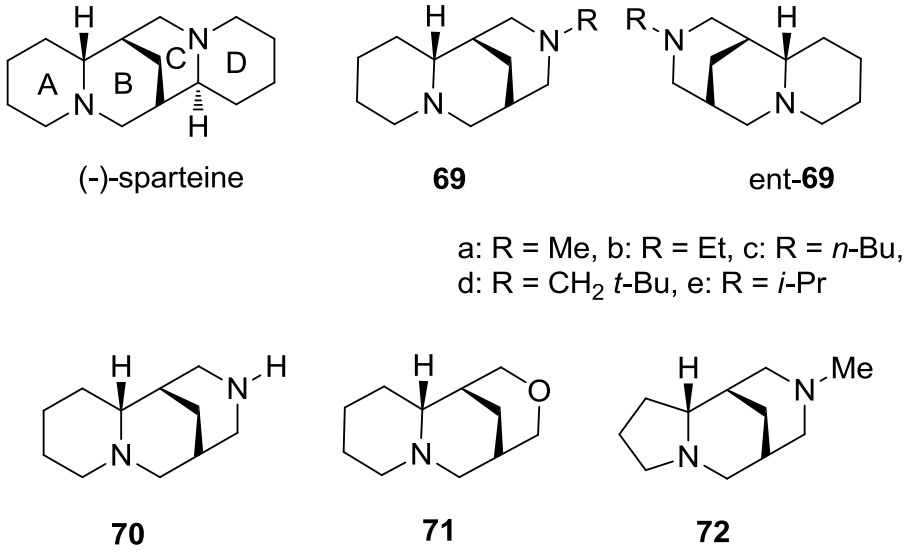
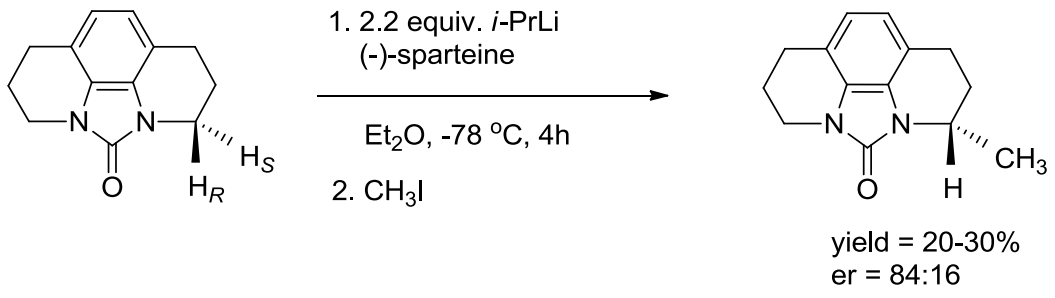


Figure 1.4. (-)-sparteine and sparteine-like ligands used in the asymmetric lithiation of *N*-Boc pyrrolidine with *i*-PrLi and *s*-BuLi.[49]

Their experimental results revealed that the *pro*-(*S*) hydrogen abstraction was favoured in the lithiation of *N*-Boc pyrrolidine when (-)-sparteine was used as the chiral ligand. On the other hand, (+)-sparteine-like chiral ligands afforded opposite enantioselectivity. In addition, it was found that the use of *i*-PrLi as the organolithium reagent resulted in higher enantioselectivity than the *s*-BuLi no matter what chiral ligand had been used. In addition, these researchers noted that the increased bulkiness of the *N*-alkyl substituent of the *ent*-**69** gave rise to lower yield and enantioselectivity after the electrophilic quench of the lithiated intermediate by TMSCl. Experimentally, the use of *N*-methyl and *N*-ethyl diamine ligand was recommended for high yield and high enantioselectivity (enantioselectivity in the opposite sense to (-)-sparteine) in such deprotonations. Their computational study started with the modeling of the *N*-Boc pyrrolidine lithiation with *i*-PrLi mediated by **69** (a, b, and c). A set of geometry optimizations were done and the *pro*-(*S*) hydrogen removal was shown to be the favoured one, which was in accordance with experimental observations obtained by *ent*-**69**a that resulted in the *pro*-(*R*) hydrogen removal. Based on their previous findings with (-)-sparteine[47] they conclude that diamine **69**a behaves the same way as (-)-sparteine in this reaction. The evaluation of the deprotonation in the presence of **69**b and **69**c produced the same results. It is noteworthy that minimum unfavourable nonbonded interactions between the *N*-ethyl and *N*-isopropyl groups and the *tert*-butoxy group of the *N*-Boc pyrrolidine were present in the lowest energy transition states for the deprotonation.

In the next part of this work, three other chiral diamines (**70**, **71**, and **72**) were subjected to computational modeling. It was suggested that **70** led to lower selectivity but the same sense of chiral induction as **69** (a, b, and c). Diamine **71** on the other hand, was found to generate small stereoselectivities and in the opposite sense to that of **69** (a, b, and c) and **70**. The last diamine (**72**) was included in the study to examine the effect of the A-ring of (-)-sparteine on the enantioselectivity of the lithiation of *N*-Boc pyrrolidine. Basically, ligand **72** represented a modification to the A and D rings of (-)-sparteine. Similar to the previous computations, corresponding deprotonation transition states were located. Calculations showed the preferential removal of the *pro*-(*S*) hydrogen, but with much lower selectivity than found with **69**a. This clearly shows the important role of (-)-sparteine's A-ring in the enantioselectiviy of the asymmetric lithiation of *N*-Boc pyrrolidine, but does not explain the detailed function of the A-ring.

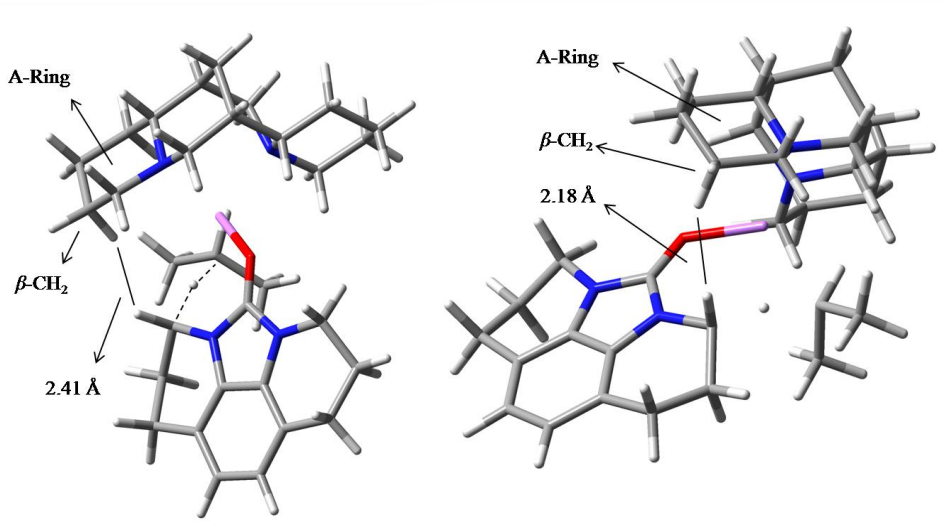
In 2004, Kozlowski *et al*. asserted that the complete A-ring of (-)-sparteine was necessary in order to achieve high levels of enantioselectivity in the asymmetric lithiation of *N*-Boc pyrrolidine.[50] Metallinos, Dudding and co-workers reported the asymmetric lithiation of **73** (**Scheme 1.17**).[51]



73 **74**

Scheme 1.17. Asymmetric lithiation/substitution of urea **73** mediated by (-)-sparteine.[51]

Compared to the asymmetric lithiation of *N*-Boc piperidine, higher yields, but lower enantioselectivities were achieved. A detailed computational study of this reaction explicitly revealed as to which portion of the (-)-sparteine's A-ring was determining the sterreoselectivity of the reaction. As such, they put forward the β-CH_2 effect theory that maintains the crucial function of this portion of (-)-sparteine's A-ring (β-CH_2) in determining the stereoselectivity of the reaction. Figure 1.5 illustrates the two lowest *pro*-(*S*) and *pro*-(*R*) transition states of the deprotonation of **73** that were located using MP2/6-31G(d)//B3LYP/6-31G(d) level of theory.



pro-(*S*)-**TS1** *pro*-(*R*)-**TS2**

Figure 1.5. Transition states leading to pro-*S* and pro-*R* hydrogen removal of **73** and demonstration of the "β-CH_2 effect".[51]

The energy difference between the two lowest diastereomeric transition states, **TS1** and **TS2**, arose from the difference in the H···H close contacts of the substrate and β-CH_2 of the (-)-sparteine's A-ring. A $\Delta\Delta E$ value of 1.26 kcal/mol translated into an enantiomeric ratio of 89:11, which was close to the experimentally observed 84:16 ratio for sequential deprotonation/methylation reaction.

The intriguing finding of β-CH_2 effect prompted us to investigate the generality of this theory in the asymmetric lithiation of other *N*-heterocycles. In doing so, the (-)-sparteine mediated asymmetric lithiation of some different *N*-heterocycles will be modelled. Subsequently, it will be shown if the β-CH_2 effect is a decicive factor by which the stereoselectivity of the lithiation reactions are determined in other structurally different *N*-heterocycles or not. Furthermore, the destabilizing influence of the D-ring of (-)-sparteine in the lowest unfavoured diastereomeric transition states was

noticed for the first time in the asymmetric lithiation of **73**. Accordingly, the stablishment of the role of this latter interaction was another theme of our research.

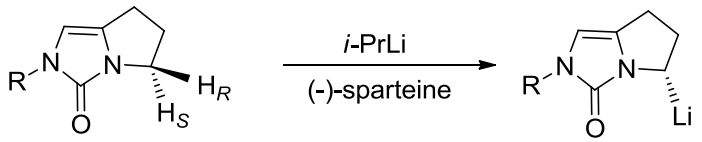
Finally, computational modelling of the asymmetric lithaition of BF_3-activated dimethylaminoferrocene will be done to gain more insights into the working features of the chiral diamine **62** which can be implemeted in the design of a new effective chiral ligand.

2. Results and Discussion

2.1 Asymmetric Lithiation of *N*-Heterocycles

2.1.a. Asymmetric lithiation of 2-tert-butyl-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-3-one (75)

Following our collaborative computational work with the Metallinos group, we set out to investigate the generality of Dudding's previously proposed model for stereoselection in (-)-sparteine mediated lithiation, which suggested that the β-CH_2 of the A ring of (-)-sparteine was the determining factor contributing to the *pro*-(*R*) versus *pro*-(*S*) enantioselectivity of the reaction.[51] More specifically, an unfavorable steric interaction between one of the β-CH_2 hydrogen(s) of the A-ring of (-)-sparteine and the α-hydrogen of the piperidyl moiety (α to nitrogen) not undergoing deprotonation was found to be the main contributor to the energy difference between the corresponding diastereomeric transition states.



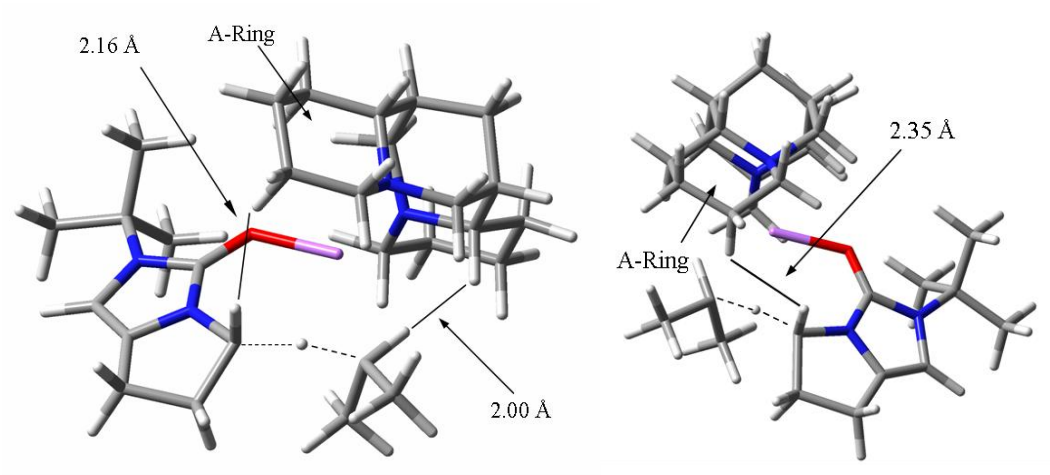
R = *t*-Bu (**73**)
R = $Si(Me)_3$ (**74**)
R = $Si(i\text{-}Pr)_3$ (**75**)

Scheme 2.1. Chemical structures of imidazolones **75**, **76,77** and their lithiated product.

To further investigate the generality of Dudding's proposal we started with computational modelling of **75** asymmetric lithiation mediated with (-)-sparteine.

Interestingly, for this case the *pro*-(*S*) hydrogen removal was found to be favoured computationally at MP2/6-31G(d)//B3LYP[52-54]/6-31G(d)[55, 56] level of theory which was in accordance with the experimental findings (**Figure 2.1**).[57] Upon close inspection of the two lowest *pro*-(*R*) and *pro*-(*S*) transition states it was revealed that the same interactions as those found in the case of the octahydrophenanthroline derived urea [51] were responsible for the energetic difference of the competing diastereomeric transition states. For the lithiation of **73** these close contact distances in the *pro*-(*R*)-TS**6** and *pro*-(*S*)-TS**4** transition states were found to be 2.16 Å and 2.35 Å, respectively (**Figure 2.1**).

Further analysis of these two stereodetermining transition states led to the finding that a second steric interaction involving the D-ring of sparteine, which had not been observed in our previous report, was also an important factor determining the stereoselection of this reaction. This second destablizing interaction involved the bridging hydrogen of the D-ring and the methine hydrogen of the *i*-PrLi was only present in the unfavored *pro*-(*R*) transition state. Therefore, it is plausible to conclude that the governing factors by which the stereoselectivity of the (-)-sparteine mediated lithiation is influenced are the A ring β-CH_2 effect and the newly found D-ring effect. All above mentioned interactions are shown in figure 2.1.



Lowest Pro-*R* transition state Lowest Pro-*S* transition state

pro-(*R*)-TS**6** $\Delta\Delta E$ = 1.61 kcal/mol *pro*-(*S*)-TS**4**

Figure 2.1. The lowest competing transition states, TS**4** (favoured) and TS**6**, in the asymmetric lithiation of **75**.

2.1.b. Asymmetric Lithiation of 2-(Trimethyl silyl)-2,5,6,7-tetrahydropyrrolo[1,2-c] imidazol-3-one (76) and 2-(Triisopropyl silyl)-2,5,6,7-tetrahydropyrrolo[1,2-c] imidazol-3-one (77)

The computational investigation of the reaction continued with the study of two other surrogates of **75**, in which the N(2) *t*-butyl group had been replaced with either a TMS (tri-methyl silyl) or TIPS (triisopropylsilyl) substituent. The reason for this substituent exchange was to evaluate the importance of the electronic effects on the yield and selectivity of the lithiation. As a matter of fact, the well known stabilization effect of the silicon atom on α-anions was used to hypothesize the influence of this stabilization on the effectiveness of the carbonyl group as a directing group. This manipulation was thought to happen through the reduced resonance of nitrogen's

electron pair with the carbonyl group. As a consequence, diminished directing power of the carbonyl would affect the stereoselectivity of the reaction. In order to put this hypothesis to test, the same computational method as the one used for **73** was exploited for the computational modeling of **76** and **77** . Hence, the relative energy values of the lowest *pro*-(*R*) and *pro*-(*S*) transition states were substituted into the equation 2.1 and the resulting values were subsequently used to compute the percent *ee* of these deprotonation reactions, assuming the Curtin-Hammett principle holds for this reaction.

$$\frac{[Diastereomer1]}{[Diastereomer2]} = \exp^{\frac{-\Delta\Delta G^{\neq}}{RT}} \qquad \frac{(1-dr)}{(1+dr)} \times 100 = \%ee$$

Equation (**2.1**)

The Curtin-Hammett principle[58] states that if a reaction includes two different interconverting intermediates, each one leading to a distinct product, the $\Delta\Delta G^{\neq}$ of each pathway can be used to determine the ratio of the products. In our case, we presume that the pre-complexes before the *pro*-(*R*) and *pro*-(*S*) transition states are in fast equilibrium and therefore the Curtin-Hammett principle is applicable to our conditions.

The MP2 single-point energy calculations revealed almost the same energy differences between the *pro*-(*S*) and *pro*-(*R*) transition states for the asymmetric deprotonations of **75**, **76** and **77**. In a similar fashion, the A ring β-CH_2 effect of 2.36 Å and 2.21Å were detected in *pro*-(*S*)-TS**8** and *pro*-(*R*)-TS**10** transitions states for **76**, respectively. Interestingly, the D-ring effect was found to be operating in the (-)-sparteine mediated lithiation of **76** as well. The 2.03 Å distance between the *i*-PrLi methine hydrogen and the methine hydrogen of the (-)-sparteine's D-ring in the *pro*-

(*R*)-TS**10** transition state of **76** clearly represents an important destabilizing element in the unfavourable transition state.

Figure 2.2 shows the competing transition state for the lithiation of **76**. Also, the MP2 energies of the computationally located transition states for the (-)-sparteine mediated lithiation of **75**, **76,** and **75** are shown in Table 2.1.

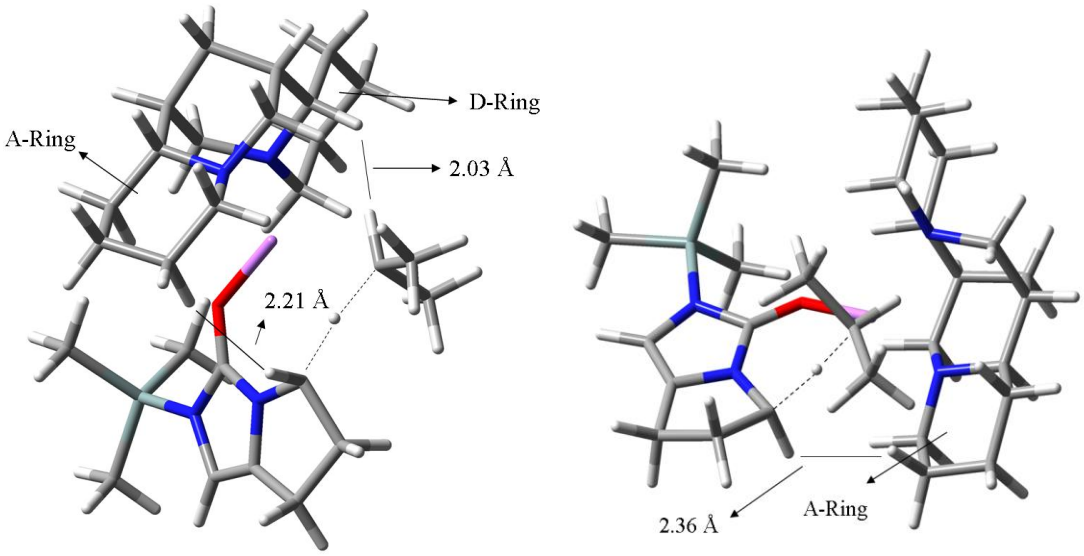
Table 2.1. The MP2/6-31G(d)//B3LYP/6-31G(d) energies (Hartrees) for the (-)-sparteine mediated deprotonation of **75**, **76**, and **77**. (*pro*-(*S*)-A-ring and *pro*-(*R*)-A-ring TSs are the lowest energy ones)

	MP2 single-point energies (Hartrees)[a]
75	
pro-(*S*)-D-ring(TS**3**)	-1393.4863791
pro-(*S*)-A-ring(TS**4**)	**-1393.4891882**
pro-(*R*)-D-ring(TS**5**)	-1393.4839435
pro-(*R*)-A-ring(TS**6**)	**-1393.4866283**
	Δ*E*=1.61 kcal/mol
76	
pro-(*S*)-D-ring (TS**7**)	-1644.5407017
pro-(*S*)-A-ring (TS**8**)	**-1644.5438096**
pro-(*R*)-D-ring (TS**9**)	-1644.5384135
pro-(*R*)-A-ring (TS**10**)	**-1644.5413158**
	Δ*E*= 1.56 kcal/mol
77	
pro-(*S*)-D-ring (TS**11**)	-1879.5208259
pro-(*S*)-A-ring (TS**12**)	**-1879.5245413**
pro-(*R*)-D-ring (TS**13**)	-1879.5204515
pro-(*R*)-A-ring (TS**14**)	**-1879.5221339**
	Δ*E*= 1.51 kcal/mol

a) Δ*E* values represent the difference between the bold numbers in the table.

Calculations of the *ee*% for the asymmetric deprotonation of **75**, **76**, and **77** were done using the MP2 single-point energies due to the reliability of this method for the

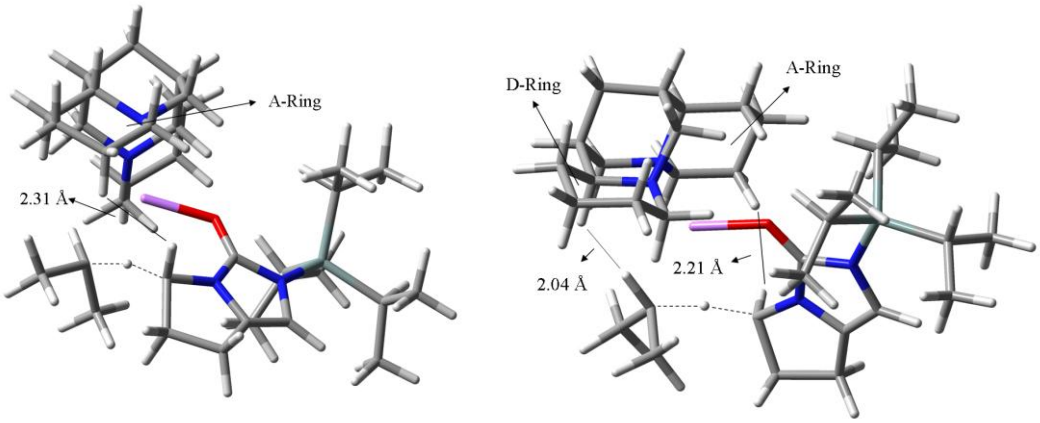
energy calculations. As such, the enantiomeric excess for the (-)-sparteine mediated lithiation of **75**, **76**, and **77** were found to be 88, 86, and 86%, respectively.



Lowest *pro*-(*R*)-TS**10** $\Delta\Delta E$ = 1.56 kcal/mol Lowest *pro*-(*S*)-TS**8**

Figure 2.2. The lowest competing transition states in the asymmetric lithiation of **76.**

The same relationships as **76** were found for **75**. The A ring β-CH_2 effect of 2.31 Å and 2.21 Å were detected in the *pro*-(*S*)-TS**12** and *pro*-(*R*) -TS**14** transition states, respectively. In addition, a D-ring effect (2.04 Å) was observed in the *pro*-(*R*)-TS**14** of **77** (**Figure 2.3**). At this point it can be concluded that alteration of the substituents at the N(2) position will insignificantly affect the stereoselectivity of the asymmetric lithiation. The slight changes in A ring β-CH_2 and D-ring effects arise from the differences in the steric and electronic properties of the N(2) substituents.



pro-(*S*)-TS**12** $\Delta\Delta E$ = 1.51 kcal/mol *pro*-(*R*)-TS**14**

Figure 2.3. The lowest competing transition states in the asymmetric lithiation of **77**.

These differences resulted in a small change in the position of the substrate with respect to the (-)-sparteine which naturally reflected itself in the final representation of the β-CH_2 and D-ring effects. As it is evidenced from the computations, the selectivities for all three cases are within a narrow range.

Finally, theoretical studies very well showed that the Dudding's proposed (-)-sparteine's β-CH_2 effect is playing a crucial role in the (-)-sparteine mediated asymmetric lithiations of **75**, **76**, and **75** as for the case of **73**. Furthermore, the preferred removal of *pro*-(*S*) hydrogen over the *pro*-(*R*) was revealed to be the fate of lithiation for **75**, **76**, and **77** as well. The consistency of our computational results with experimental observations in Metallinos group, made us confident about the competence of our method for the exploration of these kind of lithiations with the *N*-heterocycles in the presence of (-)-sparteine as the chiral ligand. The existence of all above mentioned encouraging findings intrigued us to test our computational method as well as Dudding's proposed theory by using other *N*-heterocycles as substrates.

2.1.c. Asymmetric Lithiation of N-Boc Pyrrolidine (1), N-Boc Piperidine (11)

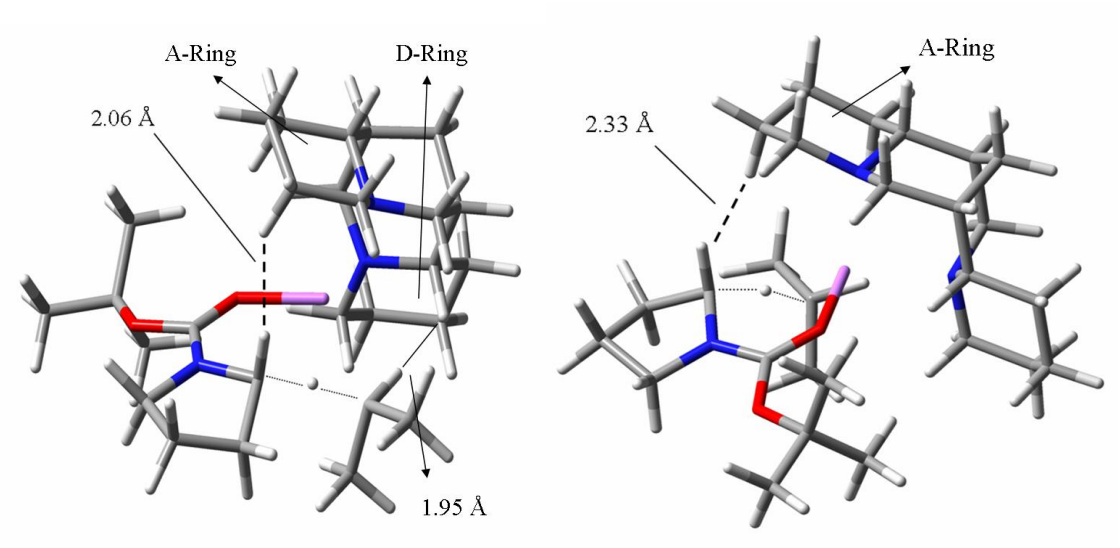
We set out to further examine our proposed theories on the origins of stereoselectivity of the asymmetric lithiations of *N*-heterocycles in the presences of (-)-sparteine as the chiral inducing amine. At this stage, we decided to start with *N*-Boc-pyrrolidine and *N*-Boc piperidine for which experimental and theoretical studies have been done by Wiberg and co-workers.[59] In this vein, based on our previous work we examined four possible modes of deprotonation corresponding to the *pro*-(*S*) and *pro*-(*R*) hydrogen removals, and the proximity of (-)-sparteine's A-ring or D-ring to the reaction center. The main reason for us to repeat the computational work on the compounds that had been already investigated by Wiberg at al. was the lack of a well theorized conclusion as to how the destiny of the reaction, in sense of stereoselectivity, is determined. We included these compounds in our research to see if any similar patterns for stereoselectivity existed. Any positive indication of a general tendency for the selectivity where (-)-sparteine was present in the asymmetric lithiation, the function of (-)-sparteine's A and D rings, would push us further toward the meaningful establishment of our proposed theory.

The transition state optimizations were done at B3LYP/6-31G(d) level of theory. Frequency computations accompanied the transition state optimizations in order to ensure the existence of an imaginary frequency, which is the exclusive characteristic of transition states, following the more accurate single-point energy calculations at

MP2/6-31G(d). A simple analysis of the obtained energy data (MP2 single-points) revealed the favoured *pro*-(*S*) proton abstraction over the *pro*-(*R*). Moreover, the possible influence of the (-)-sparteine's A and D-rings were found to be the determining factors governing the selectivity of these reactions, which was consistent with our previous findings.

As can be seen in Figure 2.4, the remoteness of the intact hydrogen of the pyrrolidine with the β-CH_2 hydrogen in the chiral ligand's A-ring is 2.33 Å in the *pro*-(*S*)-TS**16** diastereomeric transition state, whereas in the *pro*-(*R*)-TS**18** transition state it is 2.06 Å.

It is also noteworthy that the D ring effect is present in the *pro*-(*R*) transition state. This interaction exists between the methine hydrogens in *i*-PrLi and D-ring of (-)-sparteine.



pro-(*R*)-TS**18** $\Delta\Delta E$ = 2.76 kcal/mol *pro*-(*S*)-TS**16**

Figure 2.4. The lowest competing transition states in the asymmetric lithiation of *N*-Boc pyrrolidine.

The same computational method was used to evaluate the selectivity of the asymmetric lithiation in the case of *N*-Boc piperidine. As for the *N*-Boc pyrrolidine, four different diastereomeric transition states were generated as the starting geometries and submitted for the calculations. Similarly, the same behaviours and interactions were observed for this substrate. Distances of 2.32 Å and 2.23 Å represent the A-ring *β*-CH_2 effect in the *pro*-(*S*)-TS**20** and *pro*-(*R*)-TS**22** transition states, respectively. These distances are closer to each other unlike the previous lithiation cases, which agreed well with the experimentally observed lower selectivity of the *N*-Boc piperidine. [59] Wiberg et al. showed that the asymmetric lithiation of *N*-Boc piperidine with the *s*-BuLi/(-)-sparteine in a mixture of Et_2O/cyclohexane proceeded slowly and upon the substitution with TMSCl gave the desired product in low yield and modest stereoselectivity. This observed low selectivity supports our computational findings regarding the lower energy difference between the competing diastereomeric transition states (ΔE = 0.66 kcal/mol) that resulted in a 51% enantiomeric excess.

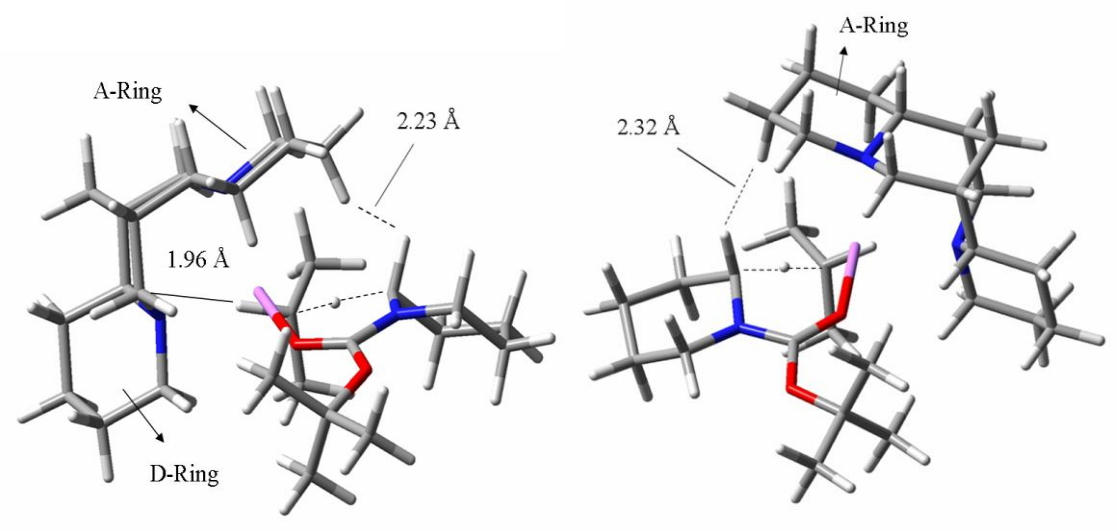
In addition, based on a detailed computational analysis made by Wiberg et al. on the removal of four different α-hydrogens of *N*-Boc piperidine, it was concluded that the least acidic equatorial hydrogen (the one closer to Boc carbonyl group) is the one involved in the proton transfer. The lowest *pro*-(*S*)-TS**20** transition state in our study represents the transfer of the least acidic equatorial hydrogen as well that is in accordance with the Wiberg's results.

Interestingly, a quick look at Figure 2.5 clearly reveals the proximity of the methine hydrogens in *i*-PrLi and D-ring of (-)-sparteine (1.96 Å), that is a manifestation of the

D-ring effect in the *pro*-(*R*)-TS**22**. This interaction can be regarded as an important element contributing to the destabilization of the *pro*-(*R*)-TS**22** diastereomeric transition state.

Outlined in Table 2.2 are the computed MP2 single-point energies of the different diastereomeric transition states for the asymmetric lithiation of *N*-Boc-pyrrolidine and *N*-Boc piperidine and the corresponding energy differences between the two lowest energy *pro*-(*R*) and *pro*-(*S*) transition states. It is noteworthy that based upon these energies the predicted *ee*s of these deprotonations were consistent with experiment.

It is worth mentioning that the competing transition states were those with the spatial arrangements that had the (-)-sparteine's A-ring proximal to the reaction center.



pro-(*R*)-TS**22** $\Delta\Delta E$ = 0.66 kcal/mol *pro*-(*S*)-TS**20**

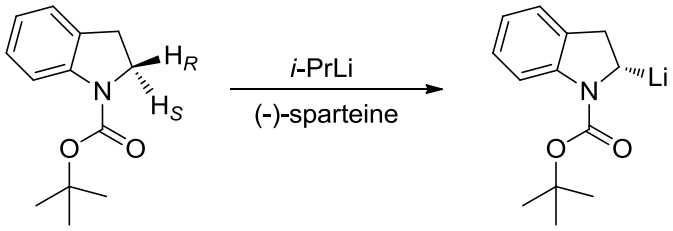
Figure 2.5. The lowest competing transition states in the asymmetric lithiation of *N*-Boc piperidine.

Table 2.2. The MP2/6-31G(d)//B3LYP/6-31G(d) energies (Hartrees) for the (-)-sparteine mediated deprotonation of *N*-Boc pyrrolidine and *N*-Boc-piperidine. (*pro*-(*S*)-A-ring and *pro*-(*R*)-A-ring TSs are the lowest energy ones)

	MP2 single-point energies (Hartrees) [a]
***N*-Boc pyrrolidine 1**	
pro-(*S*)- D-ring (TS**15**)	-1376.507933
pro-(*S*)- A-ring (TS**16**)	**-1376.513764**
pro-(*R*)- D-ring (TS**17**)	-1376.506177
pro-(*R*)- A-ring (TS**18**)	**-1376.509360**
	Δ*E*= 2.76 kcal/mol
***N*-Boc piperidine 11**	
pro-(*S*)- D-ring (TS**19**)	-1415.673418
pro-(*S*)- A-ring (TS**20**)	**-1415.678702**
pro-(*R*)- D-ring (TS**21**)	-1415.673420
pro-(*R*)- A-ring (TS**22**)	**-1415.677655**
	Δ*E*= 0.66 kcal/mol

a) Δ*E* values represent the difference between the bold numbers in the table.

2.1.d. Asymmetric Lithiation of N-Boc Indoline (78)



Scheme 2.2. Chemical structures of *N*-Boc indoline **78** and its lithiated product.

Due to the importance of chiral indolines, as mentioned in the introduction section, we included the *N*-Boc indoline **78** in our investigation of the (-)-sparteine mediated asymmetric lithiation process. Moreover, the availability of the experimental data[59] for the asymmetric lithiation of this substrate would allow us to compare our theoretical

results against them. In this vein, we constructed the four main diastereomeric transition states as well as one rotameric counterpart for each of the main structures to assess the conformational diversity of the possible transition states on a small scale. This was done by manually rotating the (-)-sparteine ligand in a manner that minimized unfavourable Van der Waals contacts, yet still allowed for deprotonation to take place. All eight structures were optimized at B3LYP/6-31G(d) and frequency calculations performed to verify the existence of deprotonation transition states. Subsequently, single-point energy calculations were carried out at MP2/6-31G(d) level of theory to obtain more dependable energies for the transition states. Table 2.3 demonstrates the energy values as well as the difference between the two lowest transition states.

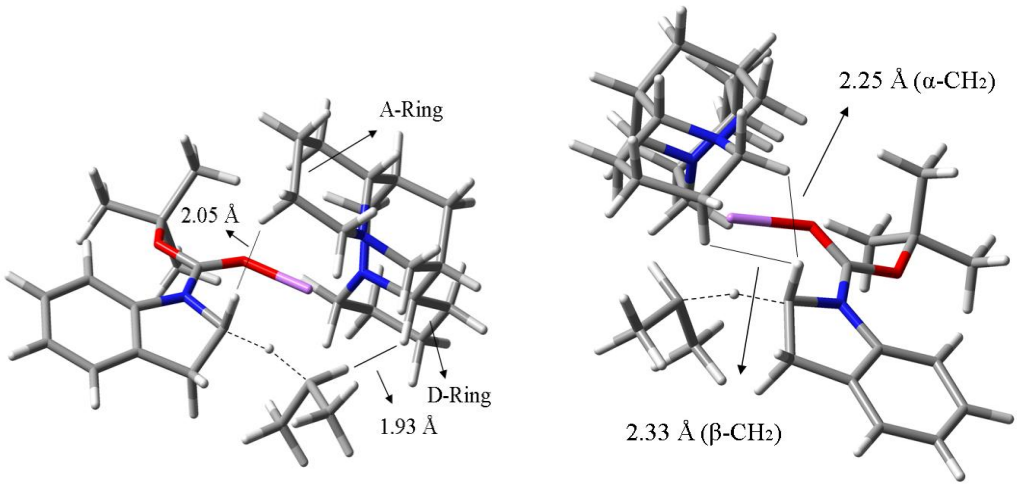
Table 2.3. The MP2/6-31G(d)//B3LYP/6-31G(d) energies (Hartrees) for the (-)-sparteine mediated deprotonation of *N*-Boc indoline. (*pro*-(*S*)-A-ring and *pro*-(*R*)-A-ring TSs are the lowest energy ones)

***N*-Boc indoline 78**	MP2 single-point energies (Hartrees) [a]
pro-(*S*)-D-ring (TS**23**)	-1528.4827052
pro-(*S*)-D-ring-rotamer (TS**24**)	-1528.4839358
pro-(*R*) -D-ring (TS**25**)	-1528.4808259
pro-(*R*) -D-ring-rotamer (TS**26**)	-1528.4835423
pro-(*S*)-A-ring (TS**27**)	**-1528.4886611**
pro-(*S*)-A-ring-rotamer (TS**28**)	-1528.4886608
pro-(*R*)-A-ring (TS**29**)	**-1528.4848133**
pro-(*R*)-A-ring-rotamer (TS**30**)	-1528.4848077
	ΔE= 2.41 kcal/mol*

a) ΔE values represent the difference between the bold numbers in the table.
*This energy difference results in a 97% *ee*.

Consistent with our previously studied cases, the inspection of all the optimized diastereomeric transition states led us to the same conclusion. In the lowest *pro*-(*R*) and *pro*-(*S*) transition states, the A-Ring portion of the (-)-sparteine resides near the position

at which hydrogen removal takes place. A close inspection of these structures revealed that the stereoselectivity of the reaction was governed by the presence of two dominant unfavourable repulsive interactions arising from the positioning of the (-)-sparteine's A-ring (**Figure 2.6**).



Pro-(*R*) TS**29** $\Delta\Delta E$ = 2.41 kcal/mol *Pro*-(*S*) TS**27**

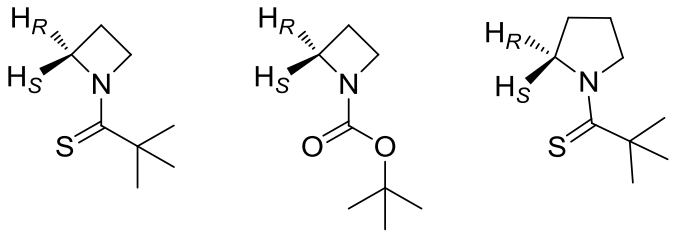
Figure 2.6. The lowest competing transition states in the asymmetric lithiation of *N*-Boc indoline.

The two major repulsive interactions in the *pro*-(*R*) transition state (2.05 Å and 1.93 Å), make the *pro*-(*R*)-TS**29** transition state higher in energy than the *pro*-(*S*)-TS**27** transition state (**Figure 2.6**). As such, it was found out that A-ring β-CH_2 effect and *D*-ring effect are the operating forces determining stereoselectivity.

Thus far, we can claim that the Dudding's proposed β-CH_2 effect of the A-ring can be generalized for the asymmetric lithiations of *N*-heterocycles conducted by (-)-sparteine. Although, it should be noted that "*Complex-Induced proximity effect*" must be happening in order to be able to make accurate predictions. The reason for this was our unsuccessful modeling of the (-)-sparteine mediated asymmetric lithiation of *N*-

thiopivaloylazetidine. The experimental results confirmed the preferable removal of the *pro*-(*R*) hydrogen over the *pro*-(*S*) that was not the outcome of our theoretical work[60]. Consequently, we argued that the total change in the working mechanism where no complexation occures, can be the rationale that explains this discrepancy.

2.1.e. Asymmetric Lithiation of N-Thiopivaloylazetidine *(79), N-Boc azetidine (80), and N*-Thiopivaloylpyrrolidine *(81)*



79 **80** **81**

Scheme 2.3. Chemical structures of **79**, **80** and **81**.

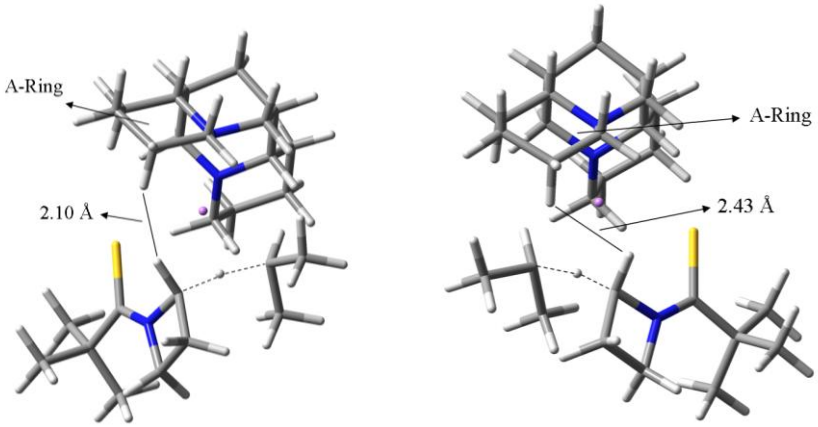
The recent report of α-CH_2 lithiation of thiopivaloyl *N*- protected azetidine in the presence of (-)-sparteine [60] intrigued us and we modelled this reaction to establish if our proposed theory was applicable to this system. Experiment showed a preference for the *pro*-(*R*) hydrogen abstraction with *s*-BuLi in different solvents. The enantiomeric excess of the reaction was less in comparison to that obtained with *N*-Boc- pyrrolidine which naturally can be thought of as resulting of weaker complexation of thiopivaloyl, lithium reagent, and the chiral base.

In a similar fashion to our previous computations we made four different *pro*-(*R*) and *pro*-(*S*) diastereomeric transition states for the asymmetric lithiation of *N*-thiopivaloyl azetidine . They were all made based on the assumption that the complexation occurred, but this interaction was less significant due to the presence of sulphur instead of oxygen. In order to obtain better starting geometries a set of optimizations were done at HF[61,62]/6-31G(d) level of theory initially. Subsequently, calculations were completed at MP2/6-31G(d)//B3LYP/6-31G(d) level to find the relevant energy values. Resulting was unfortunate finding that our theoretical results were not in agreement with the experimental evidence. More specifically, computational modeling suggested that the *pro*-(*S*) hydrogen removal was preferred, while experiments showed opposite trend.

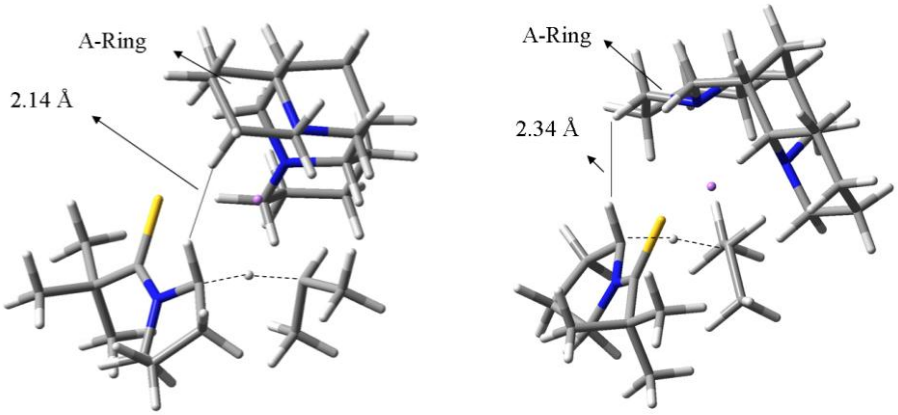
We repeated the optimization process using a diffuse-polarized basis set (B3LYP/6-31++G(2d,p) to see if the outcome changes or not and obtained the same results. This inconsistency was regarded as a rejection to the tempting speculation, according to Hodgson and Kloesges, that a ternary pre-lithiation complex consisting of the azetidine, organolithium and chiaral diamine was involved.[60] A possible explanation for this failure is to consider a lack of effective complexation due to the small ring size of azetidine. Apparently, the small ring size of azetidine modifies the hybridaztion of the ring atoms in order to lower the energy of the system caused by ring strain. This happens by increasing *p*-orbital contributions in the ring forming hybrid orbitals. Consequently, the *s* orbital character of other hybrid orbitals of ring atoms, involving nitrogen, increases. Accordingly, a higher electronegativity for nitrogen in the N-S bond is expected, which means that nitrogen will not favour its lone-pair resonance

with thiocarbonyl group. As a result, the electron density on sulphur decreases and makes the thiocarbonyl group a less effective directing group. This can be regardes as a plausible justification of the experimental findings.

At a glance it will become apparent from the transition states pictures (**Figure 2.7**) that the A-ring of the (-)-sparteine was having a key role in determinig the stereoselectivity if the complexation mechanism was working. Similarly, theoretical investigation of the asymmetric lithiation of *N*-thiopivaloylpyrrolidine with *i*-PrLi/(-)-sparteine led us to the same results and conclusion. Once more, the *pro*-(*S)* hydrogen transfer was the favourable pathway in the deprotonation reaction with the same stereodetermining elements (**Figure 2.7**).



pro-(*R*)-TS**34** ΔΔ*E*= 2.02 kcal/mol *pro*-(*S*)-TS**32**



pro-(*R*)-TS**38** ΔΔ*E*= 2.41 kcal/mol *pro*-(*R*)-TS**36**

Figure 2.7. The lowest competing transition states in the asymmetric lithiation of *N*-thiopivaloylazetidine **79** (up) and *N*-thiopivaloylpyrrolidine **81** (bottom).

All the corresponding calculated transition state energies for the aymmetric lithiation of *N*-Thiopivaloylazetidine and *N*-thiopivaloylpyrrolidine with *i*-PrLi/(-)-sparteine are listed in Table 2.4.

Table 2.4. The MP2/6-31G(d)//B3LYP/6-31G(d) energies (Hartrees) for the (-)-sparteine mediated deprotonation of *N*-Thiopivaloylazetidine and *N*-Thiopivaloylpyrrolidine. (*pro*-(*S*)-A-ring and *pro*-(*R*)-A-ring TSs are the lowest energy ones)

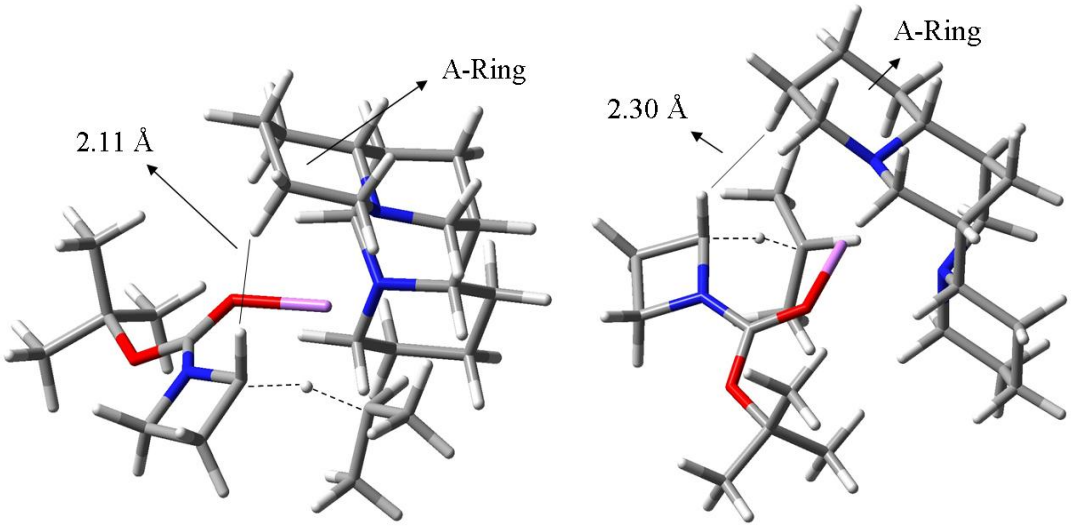
***N*-thiopivaloylazetidine 79**	MP2 single-point energies (Hartrees) [a]
pro-(*S*) - D-ring (TS**31**)	-1584.843767
pro-(*S*) - A-ring (TS**32**)	**-1584.847524**
pro-(*R*) - D-ring (TS**33**)	-1584.842493
pro-(*R*) - A-ring (TS**34**)	**-1584.844306**
	ΔE= 2.02 kcal/mol
***N*-thiopivaloylpyrrolidine 81**	
pro-(*S*) - D-ring (TS**35**)	-1624.033945
pro-(*S*) - A-ring (TS**36**)	**-1624.038398**
pro-(*R*) - D-ring (TS**37**)	-1624.033523
pro-(*R*) - A-ring (TS**38**)	**-1624.034558**
	ΔE= 2.41 kcal/mol

a) ΔE values represent the difference between the bold numbers in the table.

The next step was to make sure that the stereoselectivity was not related to the strained ring system of the azetidine. For this reason the modeling of the *N*-Boc protected azetidine was put on our to-do list to check if this one differs from other *N*-Boc protected *N*-heterocycles that we had tested before.

We made our four transition states and optimized them at B3LYP/6-31G(d) followed by MP2/6-31G(d) single-point energy calculations. Similar results were computationally produced with respect to the enantioselectivity. *pro*-(*S*) hydrogen was more favourable to be picked up by the organolithium base. Figure 2.8 clearly illustrates the same functioning causes of stereoselection that were resposnsible in previous cases. Higher repulsive interaction in the pro-*R* transition states due to the shorter distance of β-CH_2 of sparteine's A-ring and the intact α-CH_2 hydrogen of the

substrate (2.11 Å) compared to that of *pro*-(*S*) transition states is another example of the emergence of our proposed β-CH_2 effect.



pro-(*R*) TS**40** *pro*-(*S*) TS**39**

Figure 2.8. The lowest competing transition states in the asymmetric lithiation of *N*-Boc azetidine.

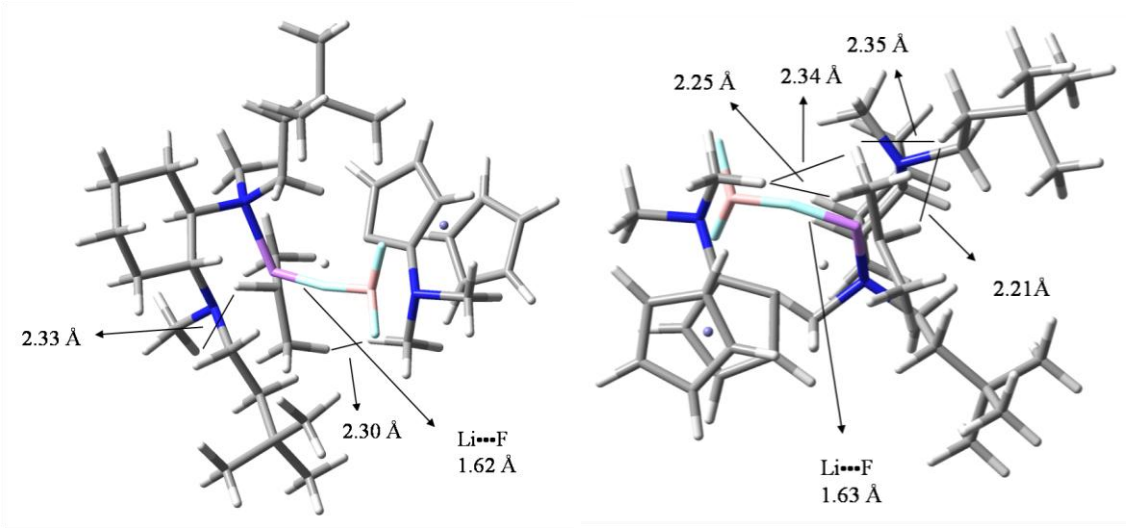
Based on the enantioselection trends that were confirmed in all of the studied cases where ternary complexation was assumed effective and the inconsistency of the compuatational and experimental results for the *N*-thiopivaloylazetidine lithiation, it can be assertively concluded that pre-lithiation complexation is not the case for *N*-thiopivaloyl protected substrates. Also, we conclude that the β-CH_2 effect of (-)-sparteine's A-ring mainly, and the D-ring effect of (-)-sparteine are the governing factors that influence the stereoselectivity in the asymmetric lithiation of *N*-heterocycles at the α-CH_2 position.

2.2 Asymmetric Lithiation of Boron Trifluoride-Activated N,N-dimethylaminoferrocene

2.2.a. Asymmetric Lithiation of Boron Trifluoride-Activated N,N-Dimethylaminoferrocene (60) in the presence of 1,2-diaminocyclohexane (R,R)-62

Another asymmetric lithiation process for which we sought to provide some mechanistic explanation was the 1,2-diaminocyclohexane (*R*,*R*)-**62** mediated asymmetric lithiation of BF_3-activated *N, N*- dimethylaminoferrocene with *i*-PrLi. This deprotonation removes the prochiral hydrogen at the sp^2 hybridized carbons lying at *ortho* position.

In order to consider all the reasonable transition states we had to envision different possibilities in constructing our transition state structures. For example, the *pro*-(*R*) or *pro*-(*S*) hydrogen abstraction, position of the lithium reagent with respect to the nitrogen substituents of the chiral ligand or the configurations at ligand's nitrogens were the factors that wee taken into account for the preparation of the starting geometries. . Considering all the possibilities we built 32 different transition states and optimized them at HF/LANL2MB[63, 64] level of theory. Subsequent single-point calculations were completed at M06-2X[65]/6-311+G (2d,2p) level of theory and the two lowest competing transition states (Figure 2.9) were identified.



pro-(*R*)-TS**41** $\Delta\Delta E$= 0.88 kcal/mol *pro*-(*S*)-TS**42**

Figure 2.9. The lowest competing transition states in the asymmetric lithiation of BF_3-activated *N, N*- dimethylaminoferrocene with *i*-PrLi/**62**. Favoured *pro*-(*R*)-TS**41** (left) and disfavoured *pro*-(*S*)-TS**42**(right).

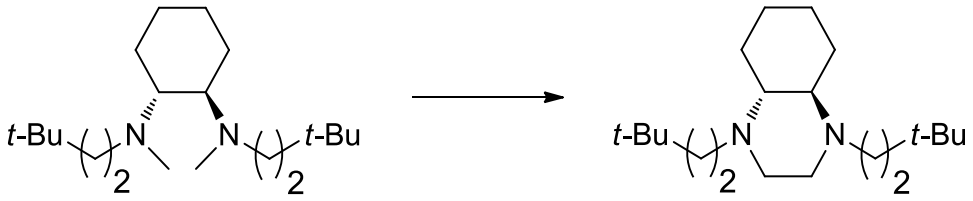
Satisfyingly, our computations produced a sense of stereoselectivity that was in full agreement with the experimentally found relative stereochemistry data. In addition, the theoretical energy difference of 0.88 kcal/mol translates to a 82:18 *er* at 25 ºC, mirroring the experimental observations. Both TSs may be viewed as eight-membered rings in slightly distorted boat-boat conformations where the aminoferrocene nitrogen and the methine carbon of *i*-PrLi occupy the apical positions. The remainder of the eight-membered transition state assemblies are comprised of lithium, fluorine, boron, prochiral Cp hydrogen, and two Cp carbons. The Li···F contact of 1.62 Å in the favoured *pro*-(*R*)-TS**41** and 1.63 Å in *pro*-(*S*)-TS**42** transition states are believed to have a crucial role in directing the lithiation process. Kessar has reported similar lithium-fluorine contacts and the presence of an eight-membered ring transition state in lithiation of BF_3-activated anilines [40]. More importantly, the orientation of the *N*-methyl

and the sterically bulky *N*-3,3-dimethylbutyl groups of the diamine ligand with respect to the activated aminoferrocene is the major diastereodifferentiating factor. For example, in the disfavoured transition state, the *N*-3,3-dimethylbutyl arms reside in a s*yn*-arrangement relative to each other and project downwards towards the *i*-PrLi reagent and the ferrocene moiety. In contrast, the *N*-3,3-dimethylbutyl groups in the favoured transition state are pointed away from the vicinity of *i*-PrLi and aminoferrocene, resulting in less steric hindrance.

In the *pro*-(*R*)-TS**41**, only two destabilizing non-bonded interactions were found: a 2.33 Å C-H···H contact between an *N*-methyl group of the ligand and *i*-PrLi, and a 2.30 Å interaction between one ferrocenyl *N*-methyl group and *i*-PrLi. Meanwhile, there are four major non-bonded interactions in the *pro*-(*S*)-TS**42** between the *i*-PrLi reagent and either the *N*-3,3-dimethylbutyl chains of the ligand (C-H···H = 2.21 Å and C-H···H = 2.35 Å), or an *N*-methyl group of the ferrocene (C-H···H = 2.25 Å and C-H···H = 2.34 Å) that favours the former one energetically.

Following our previous studies on the stereoselective lithiation of *N*,*N*-dimethylaminoferrocene using the *i*-PrLi/(*R*,*R*)-**62**, our focus then centered on designing a new ligand that coordinated more strongly and generated fewer unfavourable interactions with reagents. To this end, it was envisioned that freezing the mobility of the *N*-3,3-dimethylbutyl chains would result in the improved approach of the ligand to the substrate, which in turn would yield better chiral induction and higher selectivities. In doing so, we chose to incorporate a pipirazine ring in the ligand which we envisioned would force the 3,3-dimethylbutyl substituents to stay at the *pseudo*-

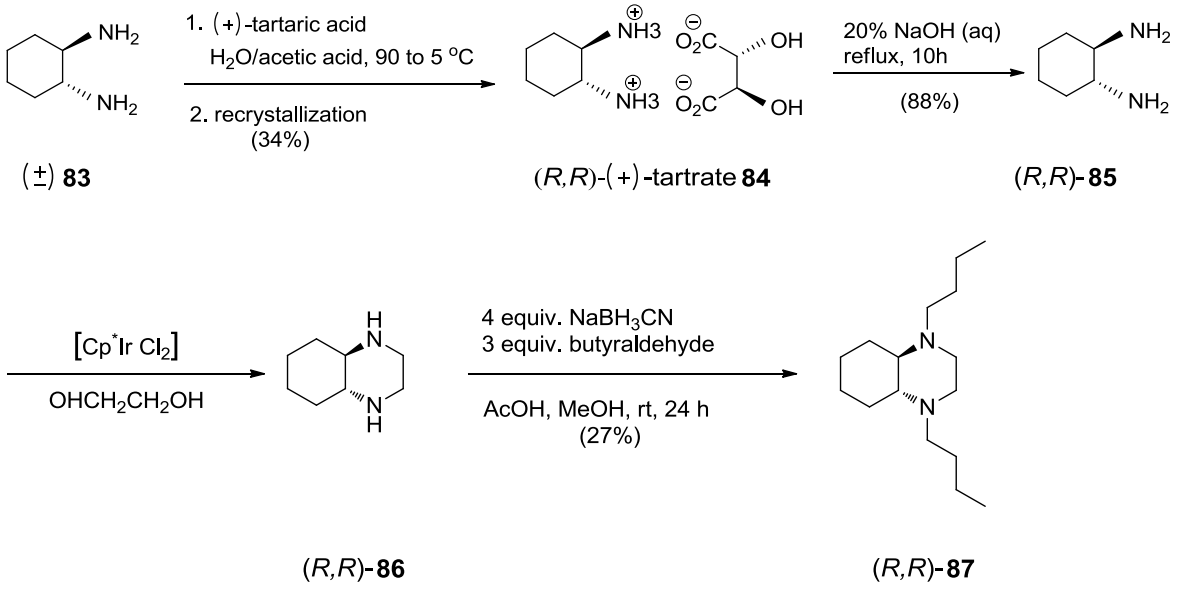
equatorial position. This way the unwanted interactions of the long chains of the new ligand and other parts of the system would be avoided (**Scheme 2.4**).



(*R*,*R*)-**62** **82**

Scheme 2.4. Simplified presentation of our rationale for the designing of new catalyst.

The experimental preparation of the new ligand was done in Metallinos's lab according to the procedure shown in Scheme 2.5.



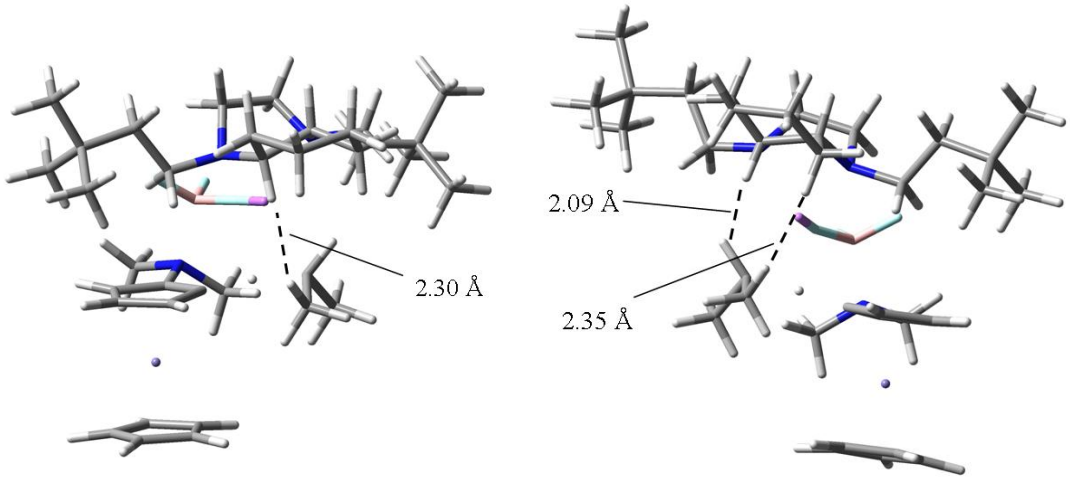
(±) **83** (*R*,*R*)-(+)-tartrate **84** (*R*,*R*)-**85**

(*R*,*R*)-**86** (*R*,*R*)-**87**

Scheme 2.5. Synthesis of *n*-Bu surrogate of **82**.

To assess the effectiveness of our subtle ligand modification and to predict the ligand's behaviour during the course of the reaction, eight different transition state structures were made and computed at the M06-2X[65]/6-311+G (2d,2p)//HF/LANL2MB level of theory. Calculations showed a preference for *pro*-(*R*) hydrogen removal over the *pro*-(*S*) hydrogen.

Further inspection of the two lowest *pro*-(*R*)-TS**43** and *pro*-(*S*)-TS**44** transition states makes it clear that confinement of the two nitrogens of the ligand in the six-membered ring successfully resulted in the elimination of the repulsive interactions between the 3,3-dimethylbutyl groups and the base. This was achieved due to the positioning of the 3,3-dimethylbutyl groups at *pseudo*-equatorial positions of pipirazine ring that resulted in their restricted movements. Furthermore, this will place the chiral centers of the new ligand to the closer proximity of the ferrocene's departing hydrogen.



$\Delta\Delta E$= 2.19 kcal/mol

Figure 2.10. The lowest competing transition states in the asymmetric lithiation of BF_3-activated *N, N*- dimethylaminoferrocene with *i*-PrLi/**80**. Favoured *pro*-(*R*)-TS**43** (left) and disfavoured *pro*-(*S*)-TS**44** (right).

A close look at the two lowest TS structures, reveals that the mean plane of the cyclohexane moiety in the ligand is roughly co-planer with the substituted cp ring. This highlights the success of our modified ligand in its approach toward the substrate. The steric interactions between the *i*-PrLi and cyclohexane component of the chiral additive, 2.30 Å in the favoured *pro*-(*R*)-TS**43** transition states and 2.35 Å and 2.09 Å in the *pro*-(*S*)-TS**44** transition state, are the main factors in differentiating the transition states energies. Moreover, it is obvious that disfavoured van der Waals contacts are less than what they were in the lithiation with the main catalyst. The calculated energy difference of 2.19 kcalmol^{-1} between the lowest competing transition states translates to a 95% *ee*.

Unfortunately, experimental endeavours by Metallinos group toward the asymmetric lithiation of *N*,*N*- dimethylaminoferrocene with the mediation of the newly designed catalyst, led to no selectivity at all. At this stage it can be concluded that our understanding of the key mechanistic elements were incorrect and need to be revised. Our approach to a new design should consider the essential role that *N*-3,3-dimethylbutyl chains play in the transmission of chiral information which were not regarded in our design (see the conclusion part).

3. Conclusions and future work

In summary, the theoretical investigations of the (-)-sparteine mediated asymmetric lithiation of some *N*-heterocyclic compounds **1**, **11**, **75**, **76**, **77**, **78**, **79**, **80**, **81** were pursued in order to understand the origin of enantioselection. Accordingly, the focus was set on the decisive function of the (-)-sparteine as the chiral inducing agent. The existence of several works through which the relationship between the structural aspects of the chiral ligands and stereoselection of the reaction had been established, gave us the idea to explain the stereoselectivity through the chiral diamine communication with the other participants. As such, the assessment of Dudding's proposed β-CH_2 effect in other cases seemed to be useful for explanation of the stereoselectivity of the asymmetric lithiation. All the studied cases uniformly showed the influential utility of the (-)-sparteines A ring. Notably, another concurrent non-bonded interaction with the involvement of (-)-sparteine's D ring and the organolithium base was discovered. It can be claimed that the placement of (-)-sparteine with respect to the base and substrate is controlled by the A and D rings of the ligand. Consequently, the outcome of the asymmetric lithiation is delicately controlled by (-)-sparteine.

The importance of the complexation on how the chiarality is induced by (-)-sparteine came to the light when the computational modeling of the (-)-sparteine conducted asymmetric lithiation of *N*-thiopivaloylazetidine gave the wrong stereoisomer. Unfortunately, attempted non-complexed based modellings were not successful and are needed to be followed for the further clarity of the (-)-sparteine's function. The non-coordinating mechanism for *N*-thiopivaloylazetidine lithiation should

be investigated if a configurationally stable anion in involved. A simple transmetallation and electrophilic quench by MeI is helpful in proving this point. On the other hand, Hodgson and Kloesges deduced the relative stereochemistry using methylated products and did not consider the possible anomalous methylation by MeI[60]. This says that other products in Hodgson work may be (*S*)-enantiomers. If this is the case, our computational results are in line with the experimental finding.

The next case was the asymmetric lithiation of *N*,*N*-dimethylaminoferrocene **60** with *i*-PrLi in the presence of (*R*,*R*)-TMCDA surrogate (*R*,*R*)-**62**. This exemplifies the hydrogen removal from prochiral sp^2 hybridized carbons. Computational modelling was started by generating 32 different transition states that were tested and the two lowest ones were further inspected for the elucidation of the stereoselectivity. The computational results mirrored the experimental observations with the preference for pro-*R* hydrogen abstraction and 82:12 *er* at room temperature. Accordingly, an argument that the placement of chiral ligand's *N*-3,3-dimethylbutyl chains was crucial to the selectivity was made. Assuming the validity of this argument, a new structural modification on the ligand was envisioned and put to the test. This design was centered on freezing the *N*-3,3-dimethylbutyl chains so that their free motions could not interfere with the ideal positioning of the chiral ligand. Subsequent computational modellings proved the effectiveness of our approach. Surprising to us, experimental utilization of the newly made ligand did not bring about compelling results and selectivities were lower that the main ligand. This clearly shows that the main principal interactions responsible for the selectivity were not those that had been highlighted in our argument of the origin of selectivity. This issue may be addressed by a new analysis of the

asymmetric lithiation of **60** in the presence of (*R*,*R*)-**62.** Apparently, chiral nitrogens on (*R*,*R*)-**62** project their chirality through the *N*-3,3-dimethylbutyl chains. Therefore, the angle they adopt within the transition state is crucial to how effectively they induce chirality in the lithiation reaction. Obviously, the nonbonded interactions of *N*-3,3-dimethylbutyl chains with the reagent and substrate, had major contributions to the oveall energy difference between the two lowest competing *pro*-(*R*) and *pro*-(*S*) diastereomeric transition states. In our design, we confined the chiaral nitrogens within a six membered ring. This approach, placed the important *N*-3,3-dimethylbutyl chains in a position where they had no possibility to transfer chiral information by having necessary interactions with the other reaction participants. In conclusion, it seems reasonable to address this problem by introducing a new linker, if we wish to have the ring in place, so that nitrogens can maintain enough flexibility to put the *N*-3,3-dimethylbutyl chains in an appropriate position.

4. Experimental

General. All the calculations were performed using the Gaussian 03 [66] and Gaussian 09 [67] suites of programs.

Lithiation Studies

a) **(-)-Sparteine Mediated Lithiations.** All corresponding transition state structures were constructed by using important metrics and insights from the previously reported computational wroks by Dudding[51] and Wiberg.[47,49] All transition state geometries were optimized in *vacuo* at B3LYP/6-31G(d) level of theory followed by the frequency calculations. All transition states were inspected by looking for one unique imaginary frequency to ensure that they were first-order saddle points. Single-point energy calculations were pursued at MP2/6-31G(d) level after each optimization to provide more reliable energy values. This level of theory was chosen due to its competence and accuracy in the computational modelling of **71**.[51] Enantiomeric excess predictions were made on the assumption that Curtin-Hammett principle was held for that reaction conditions.

b) **Asymmetric Lithiation of BF_3-Activated *N*,*N*-Dimethylaminoferrocene.** Computational modelling started with the generation of 32 unique transition state structures. For each *pro*-(*R*) and *pro*-(*S*) transition states, 16 different geometries are possible that arise from the position of BF_3 group with respect to the top Cp ring (on top or on side, 2 structures), proximity of the *i*-PrLi methyl groups to the chiral ligand (methyl groups in or out, 2 structures), and the orientation of chiral ligand's methyl (or *N*-3,3-dimethylbutyl) groups (both

pointing up or down, one pointing up and the other pointing down or vice versa, 4 structures). All transition states were optimized in *vacuo* at HF/LANL2MB level of theory followed by frequency calculations to ensure that they were first order saddle points. The reason to use this level of theory is to reduce the computational cost of study since the LANL2MB is an ECP (see appendix) basis set. Furthermore, the HF functional produces reasonable geometries while is less computationally demanding. Single-point energy calculations were carried out at M062X/6-311+G(2d,2p) level to obtain more accurate final energies. This level of theory was chosen due to its proven efficiency in dealing with the main group thermochemistry, kinetics , and noncovalent interactions.[65] Enantiomeric excess predictions were made on the assumption that Curtin-Hammett principle was held for that reaction conditions.

2-tert-butyl-2,5,6,7-tetrahydropyrrolo[1,2-c] imidazol-3-one (75)

Structure: TS3

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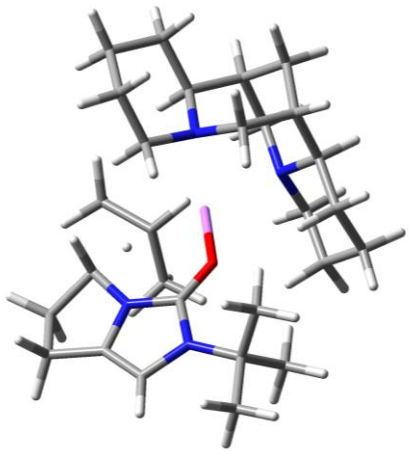

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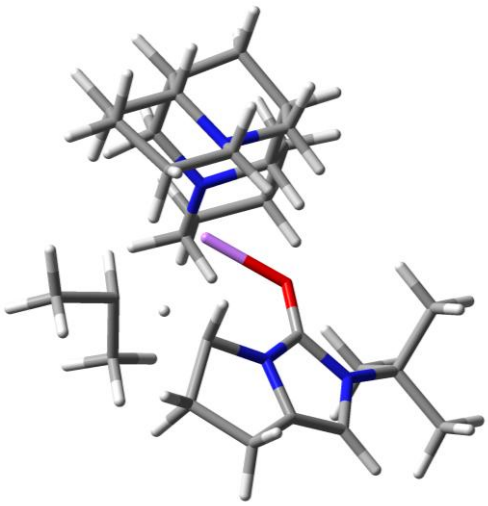

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Structure: TS5

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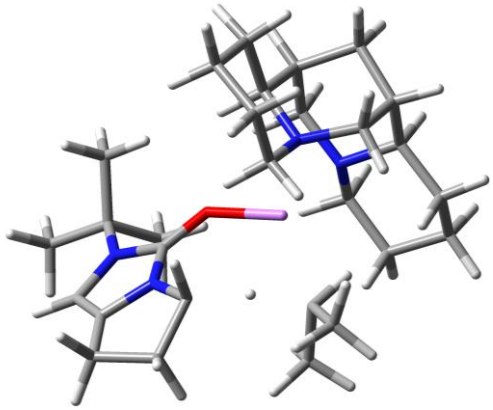

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C	1.57574800	-2.61864500	2.53414000
H	3.11786600	-2.10796500	3.98148300
H	3.65529700	-3.19801300	2.70404600
H	1.32920900	4.48237500	-1.64809900
H	2.90797700	3.70398000	-1.66662200

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 H                     0.92821100   -1.80823900    2.88601800
 H                     1.23201000   -3.53802900    3.02452100
```

Structure: TS6

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 ******************************************
 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
               26-Aug-2009
 ******************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=AM64L-G03RevD.01\State=1-A\HF=-1388.916951\MP2=-
1393.4866283\RMSD=5.726e-09\Thermal=0.\PG=C01 [X(C28H49Li1N4O1)]\\@
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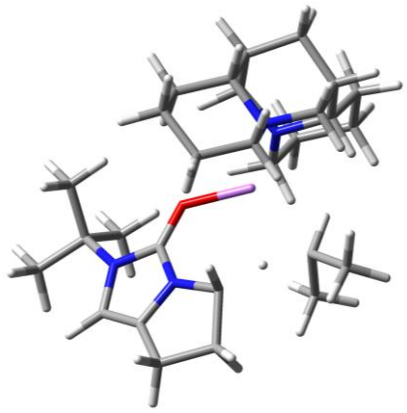

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0 1
 C                    -2.25109800    0.27539600    0.04206900
 N                    -3.35293200    1.11285900    0.18146100
 N                    -2.74745500   -0.92441400   -0.34068700
 C                    -4.12689300   -0.86202400   -0.49173000
 C                    -4.51578200    0.39421400   -0.17222800
 H                    -5.49091100    0.84854700   -0.16646600
 C                    -3.27693800    2.55437400    0.53892000
 C                    -4.62196300   -2.19466100   -0.97020900
 H                    -5.42210900   -2.11773500   -1.71428600
 H                    -5.00874100   -2.79031500   -0.13024200
 C                    -2.13329800   -2.21201300   -0.72404600
 C                    -3.30003800   -2.81786500   -1.53726900
 H                    -3.30675000   -3.91182200   -1.48907400
 H                    -3.22039800   -2.53887300   -2.59646900
 C                    -2.60225800    2.69728600    1.91651400
 H                    -1.59814100    2.27039000    1.89751400
 H                    -3.18778300    2.18105500    2.68552500
 H                    -2.53163700    3.75606600    2.19125800
 C                    -4.69333900    3.14520600    0.61290400
 H                    -5.30820600    2.63444900    1.36171600
 H                    -5.20618600    3.10264000   -0.35367400
```

H	-4.61911900	4.19805300	0.90304500
C	-2.47335500	3.29940700	-0.54399000
H	-2.39952000	4.36478700	-0.29690400
H	-2.96442400	3.20490600	-1.51884300
H	-1.46611000	2.88550100	-0.62129400
O	-1.03350200	0.57220000	0.24315400
H	-2.00505400	-2.79672700	0.20182700
C	0.31173500	-1.83033700	-2.20685000
H	1.28208400	-1.32895100	-2.02627200
C	0.59846900	-3.32191000	-2.40022000
H	-0.34397900	-3.89301800	-2.40848900
H	1.20430100	-3.73663500	-1.58043500
H	1.12200900	-3.56357100	-3.34151100
C	-0.29416200	-1.22071500	-3.47696800
H	-0.44327300	-0.13474800	-3.38471300
H	-1.28515100	-1.65376700	-3.67493900
H	0.30749500	-1.39137500	-4.38745900
Li	0.46655500	-0.49505500	-0.29123200
H	-0.82973500	-1.92882400	-1.34112700
H	4.71935500	-0.41132700	2.15865100
C	4.23670600	0.20961200	1.39286600
C	3.92109500	-0.62590400	0.14526800
C	2.89064500	0.73804400	1.90250200
H	4.92702300	1.03000100	1.16798200
C	3.34652700	0.27519700	-0.96895600
C	3.00185900	-1.79622700	0.55119300
H	4.83946000	-1.07971900	-0.25055700
C	2.24947700	1.62790200	0.81595700
C	2.05113300	-0.46695200	2.37945900
H	3.04614700	1.37742800	2.78181900
N	2.11076400	0.95678600	-0.49629300
C	4.40462700	1.23887100	-1.55537400
H	3.02586900	-0.37320500	-1.79671100
N	1.75863500	-1.40135100	1.25956800
H	2.71119000	-2.37554300	-0.33183800
H	3.59395900	-2.46985300	1.19986500
H	2.86010200	2.54447500	0.74449300
H	1.24409600	1.93986000	1.11739600
H	2.69056400	-1.00109100	3.11449600
C	0.76401900	-0.07742100	3.11683800
C	1.56624700	1.86194900	-1.53411200
H	5.23472000	0.64361000	-1.95828200
H	4.83057500	1.87614300	-0.77020100
C	3.80417500	2.13265900	-2.64938700
C	1.09839300	-2.62573700	1.77036700
H	0.08432800	0.44040600	2.43101700
H	1.02227200	0.61981600	3.92489500
C	0.06777100	-1.32227600	3.67910700
H	0.69547400	2.36775600	-1.10674600
C	2.57330200	2.87022700	-2.10799000
H	1.19790400	1.23021400	-2.35337400
H	3.50611700	1.51225000	-3.50724100
H	4.55536700	2.84150800	-3.01902200
H	0.87847500	-3.26919300	0.91162700
H	1.80140000	-3.17837300	2.42435700
C	-0.18484800	-2.32212600	2.54678900
H	-0.87549500	-1.04978700	4.16784600

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 H                     0.70348100   -1.78295100    4.44983300
 H                     2.08428600    3.45069900   -2.90052400
 H                     2.87990100    3.58941400   -1.33602300
 H                    -0.93439300   -1.91240300    1.86247100
 H                    -0.58882000   -3.26483100    2.93667300
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2-(trimethyl silyl)-2,5,6,7-tetrahydropyrrolo[1,2-c] imidazol-3-one (76)

Structure: TS7

```
*****************************************
 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
                26-Aug-2009
 *****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=AM64L-G03RevD.01\State=1-A\HF=-1640.0301447\MP2=-
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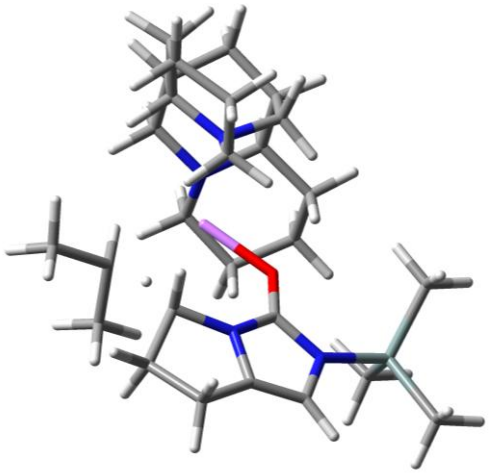

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0 1
 C                     2.07055300    0.46494600   -0.17296100
 N                     3.35528300    0.03621400   -0.50387600
 N                     2.16093700    1.79089900    0.06811900
 C                     3.48128600    2.22148600   -0.05269900
 C                     4.22685300    1.15190700   -0.40886800
 H                     5.28479500    1.05353400   -0.59177100
 C                     3.54403900    3.68068200    0.28965000
 H                     3.54966300    4.29337900   -0.62371200
 H                     4.43210800    3.94985900    0.87164500
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C	1.20588200	2.82909900	0.50046300
H	0.75684500	3.24692800	-0.41664000
C	2.19921900	3.86315800	1.07571900
H	2.39555200	3.66412000	2.13792300
H	1.81439800	4.88563000	1.00201700
C	3.56790800	-2.73890900	0.60269800
H	3.78313400	-3.79087900	0.37709100
H	2.53740100	-2.67122800	0.96409200
H	4.23049600	-2.42730800	1.41849000
C	5.63001400	-1.59931500	-1.40039800
H	5.95960300	-2.60515200	-1.68892100
H	6.27239900	-1.27130000	-0.57519400
H	5.81020900	-0.93787200	-2.25555800
C	2.76195800	-2.23050000	-2.36754600
H	2.98769000	-3.27254700	-2.62593900
H	2.95099600	-1.61587600	-3.25546100
H	1.69683700	-2.15911600	-2.12812100
O	1.03394200	-0.26530100	-0.12628200
H	0.16507400	2.18525900	1.30978100
C	-0.77523000	1.79933800	2.32526200
H	-1.56151600	1.02182200	2.28892200
C	0.13058400	1.49275800	3.52361400
H	0.56793200	0.48490300	3.46343500
H	-0.37571400	1.56920200	4.50254300
H	0.97575600	2.19613000	3.55619800
C	-1.48479600	3.14488500	2.49563100
H	-2.27758700	3.28773100	1.74581000
H	-0.77251000	3.97421100	2.35715500
H	-1.94792600	3.28862000	3.48721900
Li	-0.67654200	0.23131300	0.60848400
H	-0.01743800	-2.41006200	-0.27212000
C	-0.74077300	-3.14933100	0.08707800
C	-2.12574400	-2.50236600	0.21714700
H	-0.80017400	-3.95053400	-0.66156000
C	-0.26716100	-3.70620100	1.43577000
N	-2.10801400	-1.41808700	1.23546400
H	-2.81853000	-3.29549700	0.57122700
C	-2.71576200	-2.00431600	-1.12286900
C	-0.29957500	-2.59683200	2.49315600
H	0.74103800	-4.12722300	1.34566100
H	-0.92638900	-4.52983800	1.74776200
C	-3.45180000	-0.81263200	1.38467900
C	-1.68189800	-1.94583600	2.55077100
C	-1.95991000	-0.85445100	-1.81982200
H	-2.69256400	-2.86055700	-1.81059000
C	-4.16460200	-1.56368400	-0.88321700
H	0.45260300	-1.83474800	2.25238200
H	-0.05237100	-2.99205300	3.48620400
H	-3.36311400	0.03165200	2.07743100
H	-4.13594400	-1.54505800	1.85510000
C	-4.09448300	-0.35668200	0.06261000
H	-1.68361100	-1.11187800	3.26077700
H	-2.42142600	-2.68710400	2.91289000
N	-2.01202800	0.42341300	-1.07621900
H	-2.38417300	-0.75733600	-2.83429000
H	-0.90027400	-1.10228900	-1.94246300
H	-4.74421200	-2.37417500	-0.42256800

```
 H                  -4.66136200   -1.31377300   -1.82733100
 C                  -3.37114800    0.82682500   -0.61859500
 H                  -5.10668400   -0.01183100    0.31242300
 C                  -1.33913900    1.52319300   -1.80479300
 C                  -4.23787200    1.46241800   -1.73348300
 H                  -3.20363800    1.60570600    0.14020900
 H                  -0.37003900    1.14717600   -2.14749500
 C                  -2.14911300    2.12825200   -2.96015500
 H                  -1.13209400    2.31436400   -1.07407300
 H                  -5.17562800    1.81871800   -1.28705700
 H                  -4.51410600    0.70658900   -2.47967500
 C                  -3.50873400    2.61134700   -2.44183000
 H                  -1.57926000    2.95744100   -3.39806600
 H                  -2.29439300    1.38980100   -3.76084400
 H                  -3.35381100    3.43982700   -1.73531800
 H                  -4.12464100    3.00576900   -3.25950100
 Si                  3.80772200   -1.64979600   -0.91369900
```

Structure: TS8

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*****************************************
 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
               26-Aug-2009
 *****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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Version=AM64L-G03RevD.01\State=1-A\HF=-1640.0319923\MP2=-1644.5438096\
RMSD=5.442e-09\Thermal=0.\PG=C01 [X(C27H49Li1N4O1Si1)]\\@
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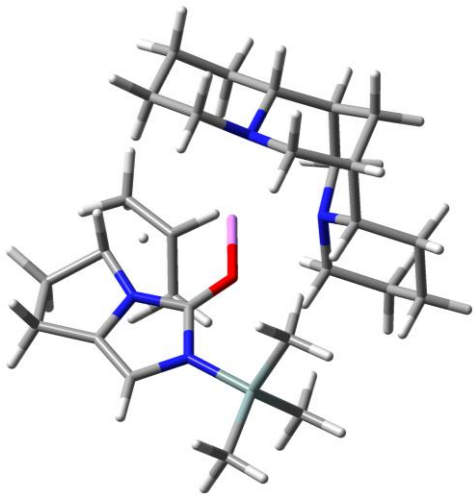

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0 1
 C                   2.08044400    0.41116700   -0.25473800
 N                   3.35623500   -0.13448800   -0.37427200
 N                   2.24505300    1.74310400   -0.11790500
```

C	3.59794100	2.07303500	-0.11405100
C	4.29526400	0.92501300	-0.27374400
H	5.35626800	0.73740800	-0.31212400
C	3.72691100	3.55575300	0.07745100
H	3.89608900	4.05569100	-0.88731700
H	4.55137100	3.83671800	0.74144000
C	1.31925800	2.86588600	0.10329500
H	0.96250400	3.18839000	-0.88931100
C	2.31329600	3.91439000	0.65559000
H	2.36854900	3.85408600	1.75061700
H	2.01350300	4.93682400	0.40317900
C	3.06730300	-2.83116800	0.89334400
H	3.22357600	-3.91075700	0.77610700
H	1.99603500	-2.65219000	1.02973200
H	3.58044200	-2.51333700	1.80828200
C	5.57127000	-2.03425700	-0.74959900
H	5.84178300	-3.08568700	-0.90715500
H	6.08717200	-1.69736500	0.15684300
H	5.96681900	-1.46432500	-1.59815800
C	2.86204100	-2.45871200	-2.18968300
H	3.00940900	-3.53448000	-2.34650800
H	3.26695400	-1.93312800	-3.06231100
H	1.78594900	-2.26259000	-2.14784600
O	0.98725200	-0.23149800	-0.28661000
H	0.23877500	2.35943600	0.95503800
C	-0.65342900	2.02803300	2.05312100
H	-1.51226300	1.32443800	2.05658000
C	0.31044000	1.60108000	3.16864700
H	0.68362800	0.57673700	3.02904100
H	-0.12628400	1.65305900	4.18222000
H	1.19499100	2.25421600	3.18009700
C	-1.21728400	3.42375100	2.33668800
H	-1.58540900	3.55564900	3.36894700
H	-2.04905700	3.67878700	1.66515900
H	-0.44309400	4.19139800	2.17867800
Li	-0.69635400	0.51012600	0.30482500
H	-3.30620700	1.92794400	0.64618000
C	-3.85062400	1.91490400	-0.30495300
C	-3.50290500	0.64250900	-1.08703000
H	-4.92247600	1.90010500	-0.06722100
C	-3.49448900	3.16826500	-1.11354000
N	-2.05290800	0.61424600	-1.41631500
H	-4.07129300	0.68606500	-2.04024800
C	-3.95949100	-0.66189100	-0.39575800
C	-2.02205900	3.11429000	-1.53506000
H	-3.69214400	4.07289500	-0.52631800
H	-4.13683900	3.22129000	-2.00504600
C	-1.68379000	-0.61269300	-2.16355700
C	-1.69264700	1.79420000	-2.23503500
C	-3.30321300	-0.98051200	0.96273500
H	-5.03631300	-0.55299300	-0.20835300
C	-3.70939800	-1.83072500	-1.35573400
H	-1.38129600	3.22587900	-0.65471700
H	-1.78055700	3.94139300	-2.21471400
H	-0.59213200	-0.62560500	-2.24537800
H	-2.09695500	-0.55894700	-3.18912900
C	-2.18753600	-1.92326500	-1.52831600

H	-0.61940200	1.73537700	-2.44927300
H	-2.22301600	1.74578000	-3.20644700
N	-1.85877100	-1.27624800	0.86106400
H	-3.86571800	-1.82039000	1.40595800
H	-3.41169000	-0.13601800	1.65299700
H	-4.19315800	-1.64369200	-2.32328000
H	-4.13221000	-2.76206700	-0.96277100
C	-1.51046000	-2.28053200	-0.18535900
H	-1.93493200	-2.72471400	-2.23569600
C	-1.26589200	-1.63911000	2.16869400
C	-1.79996300	-3.74041400	0.23683600
H	-0.42554100	-2.18741800	-0.31898500
H	-1.59170900	-0.89499500	2.90277000
C	-1.57738200	-3.06445300	2.64877600
H	-0.17806900	-1.53136100	2.06701600
H	-1.42873200	-4.41170100	-0.54903400
H	-2.88069600	-3.91629200	0.31003600
C	-1.15051200	-4.08265300	1.58462300
H	-1.05301800	-3.24421200	3.59588600
H	-2.64997800	-3.17338400	2.86031500
H	-0.05582300	-4.06002800	1.48101200
H	-1.41609800	-5.10273800	1.88901500
Si	3.69667900	-1.87965600	-0.60409000

Structure: TS9

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*****************************************
 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
               26-Aug-2009
 *****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=AM64L-G03RevD.01\State=1-A\HF=-1640.0291229\MP2=-
1644.5384135\RMSD=5.253e-09\Thermal=0.\PG=C01 [X(C27H49Li1N4O1Si1)]\\@
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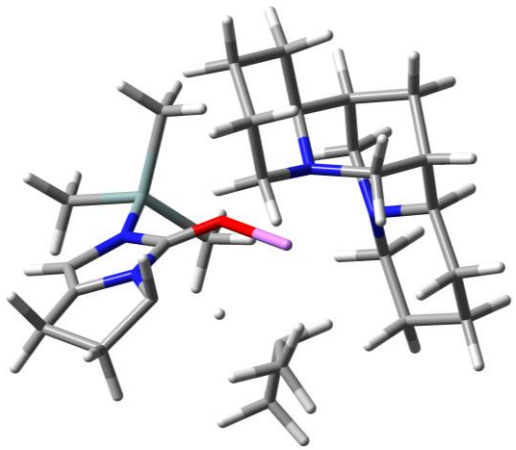

0 1

C	2.13974700	0.16366700	0.06599500
N	3.36417200	-0.49654000	0.14320900
N	2.41726600	1.48418500	0.03305500
C	3.79489300	1.69457200	0.05040000
C	4.39061300	0.48286200	0.12119300
H	5.43198500	0.20449500	0.14201800
C	4.05575500	3.16914500	-0.03766200
H	4.91004600	3.42012300	-0.67554800
H	4.25544200	3.58607500	0.96026200
C	1.59915600	2.70400600	-0.10092000
C	2.68495000	3.68678200	-0.59614500
H	2.47716400	4.71633000	-0.28656300
H	2.74109300	3.68232600	-1.69282300
C	2.67026400	-2.89997100	1.78350800
H	1.61941600	-2.59441800	1.76783100
H	3.12609900	-2.49300500	2.69368900
H	2.70899100	-3.99445300	1.84858500
C	5.41528500	-2.58852800	0.38965500
H	5.84477000	-2.11093700	1.27772700
H	5.96590500	-2.23238900	-0.48849700
H	5.60048800	-3.66635700	0.47586400
C	2.88107900	-3.07130800	-1.31966800
H	2.97499800	-4.16379700	-1.28394200
H	3.41819900	-2.71564300	-2.20646900
H	1.82276800	-2.82380000	-1.44728300
O	0.99926400	-0.39285500	0.04876400
H	1.29433500	2.99727900	0.91794200
C	-0.57942200	2.24035900	-1.93440900
H	-1.43461700	1.53755000	-2.00118900
C	-1.16933400	3.65092800	-1.85716000
H	-1.94338000	3.73201800	-1.08001800
H	-1.62413600	4.00145500	-2.80012600
H	-0.38566300	4.38049400	-1.59546500
C	0.26322500	2.07021600	-3.20464900
H	0.65600800	1.04802400	-3.31032600
H	1.13907500	2.73391100	-3.17226200
H	-0.27467400	2.31147200	-4.13901900
Li	-0.65853300	0.41939000	-0.48032600
H	0.43584200	2.35260500	-0.91691600
H	-4.14460200	-2.65956100	1.11729900
C	-3.73885600	-1.68318500	1.41213700
C	-2.21682800	-1.76748800	1.58801400
C	-3.98449300	-0.64388100	0.31224000
H	-4.24130700	-1.39748200	2.34293900
C	-1.65597300	-0.42597600	2.11184800
C	-1.59312400	-2.23778400	0.25938800
H	-1.96365300	-2.53210700	2.33472700
C	-3.44358300	0.71949100	0.78943200
C	-3.40248400	-1.18785900	-1.01192500
H	-5.06328700	-0.51587300	0.14993700
N	-2.02053000	0.68936800	1.19117200
C	-2.05043300	-0.17248200	3.58711700
H	-0.55923400	-0.48116400	2.07384900
N	-1.93398500	-1.39567500	-0.91326500
H	-0.50263400	-2.25684300	0.33718400
H	-1.93672600	-3.27487800	0.07883700

H	-4.09463600	1.05185600	1.61652800
H	-3.53774300	1.47265700	-0.00110200
H	-3.87932900	-2.18078800	-1.15977900
C	-3.76112300	-0.34544800	-2.24255200
C	-1.56594500	1.99626300	1.71986200
H	-1.65060100	-0.99169200	4.19957500
H	-3.14106000	-0.19878600	3.70649200
C	-1.53041400	1.17935300	4.09321100
C	-1.42545100	-2.06357200	-2.13116700
H	-3.34176600	0.66263500	-2.14486800
H	-4.85299500	-0.23775300	-2.28378800
C	-3.23822600	-0.99599700	-3.52956600
H	-1.90509900	2.77309600	1.02774700
C	-2.00019000	2.30179500	3.16084900
H	-0.47078000	1.99947900	1.67932300
H	-0.43074400	1.16478100	4.11623300
H	-1.86525500	1.35572500	5.12293600
H	-0.34335200	-2.18605200	-2.01292100
H	-1.86314300	-3.07874600	-2.20836500
C	-1.73640100	-1.27846500	-3.40635800
H	-3.43894800	-0.35183800	-4.39378900
H	-3.77665700	-1.93924900	-3.70447900
H	-1.57458600	3.26711900	3.46248600
H	-3.09205800	2.40717800	3.22396900
H	-1.18270600	-0.33352200	-3.39991200
H	-1.37724800	-1.85264200	-4.26965500
Si	3.56049200	-2.27604100	0.24548500

Structure: TS10

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 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
               26-Aug-2009
 *****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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Version=AM64L-G03RevD.01\State=1-A\HF=-1640.0303566\MP2=-1644.5413
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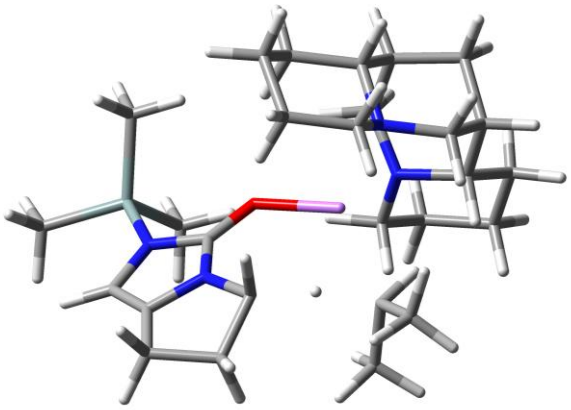

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N	3.31009100	-0.66420400	-0.08099700
N	2.51588200	1.37727200	-0.27779200
C	3.89400500	1.45864500	-0.47087600
C	4.39644200	0.20969800	-0.34851900
H	5.40450600	-0.16174300	-0.43858800
C	4.25403600	2.88579600	-0.76050300
H	5.02525300	2.98921800	-1.53141400
H	4.62590200	3.38277500	0.14737100
C	1.78645300	2.65007700	-0.43540600
C	2.86165600	3.46769800	-1.18647500
H	2.78155900	4.53962100	-0.97791500
H	2.75796000	3.33819400	-2.27214300
C	2.67426100	-2.83356400	1.88833800
H	1.63133200	-2.50898700	1.95316200
H	3.23400500	-2.32730700	2.68333100
H	2.71011100	-3.91212400	2.08680700
C	5.22729700	-2.87859400	0.14116000
H	5.80295400	-2.34824200	0.90827400
H	5.67799600	-2.66039400	-0.83381600
H	5.35035400	-3.95325600	0.32377800
C	2.47076900	-3.33892500	-1.17383400
H	2.54373100	-4.42608700	-1.04485700
H	2.88076300	-3.08865500	-2.15903200
H	1.41071600	-3.06801500	-1.17288700
O	0.96933700	-0.34730700	0.12313500
H	1.65730500	3.07377900	0.57481400
C	-0.72634700	2.33968400	-1.81877000
H	-1.63009300	1.71139100	-1.69838600
C	-1.15886900	3.79954000	-1.65748900
H	-0.27442400	4.45314900	-1.58431100
H	-1.74052700	3.96066700	-0.73753000
H	-1.76736200	4.18531300	-2.49386100
C	-0.17493200	2.08980200	-3.22796100
H	0.08085600	1.03288400	-3.39329000
H	0.75173000	2.66080400	-3.38326200
H	-0.86392000	2.38899200	-4.03777500
Li	-0.64884300	0.64755900	-0.20041300

H	0.47362100	2.36398600	-1.02773100
H	-4.74927000	-0.49970200	2.22932800
C	-4.21131800	-0.88554400	1.35377200
C	-4.07771400	0.20517800	0.28297700
C	-2.78150700	-1.28601900	1.73522500
H	-4.77949900	-1.74676800	0.98536400
C	-3.42038200	-0.37105700	-0.98964100
C	-3.32636100	1.40732900	0.89236400
H	-5.06964200	0.57673900	-0.00692000
C	-2.06783400	-1.85403200	0.48899200
C	-2.10739100	-0.07589100	2.41827300
H	-2.80317800	-2.09245700	2.48063900
N	-2.08065800	-0.93252700	-0.66957100
C	-4.34485200	-1.35947900	-1.74001200
H	-3.23212000	0.46316500	-1.68078000
N	-2.00701400	1.08292500	1.49053600
H	-3.16558200	2.18089800	0.13342500
H	-3.98153900	1.84651500	1.66889500
H	-2.54904500	-2.81832300	0.25113300
H	-1.01705400	-2.06879600	0.70850500
H	-2.78470900	0.20910000	3.25176200
C	-0.74355300	-0.39219600	3.04522800
C	-1.44765200	-1.52531700	-1.86904100
H	-5.26963800	-0.83473600	-2.01425200
H	-4.64029700	-2.19013200	-1.08633700
C	-3.66046500	-1.93005800	-2.99025500
C	-1.51094200	2.27761800	2.21200100
H	-0.03133700	-0.67564900	2.26247700
H	-0.86188300	-1.25083300	3.71967600
C	-0.20052600	0.82170000	3.80900100
H	-0.48891800	-1.95045900	-1.55890400
C	-2.31106000	-2.55451000	-2.61387000
H	-1.22067900	-0.69863400	-2.55536500
H	-3.49419000	-1.12215400	-3.71774800
H	-4.31097600	-2.66561200	-3.47932800
H	-1.44003000	3.09753900	1.48943100
H	-2.24999900	2.57950200	2.98025500
C	-0.15502300	2.03818700	2.87851100
H	0.79694400	0.60825300	4.21191100
H	-0.85127100	1.03739500	4.66952500
H	-1.77275700	-2.89193900	-3.50856400
H	-2.47333900	-3.44484900	-1.99077000
H	0.60587000	1.88058100	2.10686200
H	0.13040000	2.94362300	3.42857600
Si	3.39426900	-2.43429900	0.19501800

2-(triisopropyl silyl)-2,5,6,7-tetrahydropyrrolo[1,2-c] imidazol-3-one (77)

Structure: TS11

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 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
               25-Aug-2009
 *****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=AM64L-G03RevD.01\State=1-A\HF=-1874.2000751\MP2=-
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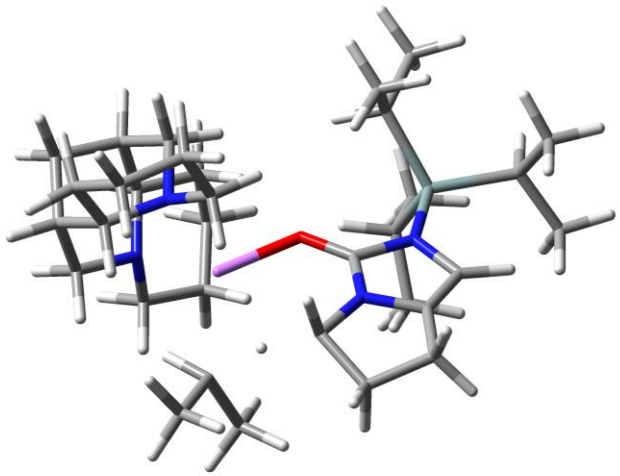

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 C                  1.19924700    1.10154900   -0.00890900
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 C                  2.16579400    3.13695300    0.08809600
 C                  3.15826100    2.24690700   -0.13413000
 H                  4.22140200    2.38919000   -0.22588600
 C                  1.87289200    4.58954800    0.32042800
 H                  1.83220900    5.13426200   -0.63411400
 H                  2.62006800    5.08535200    0.94955900
 C                 -0.22698400    3.23950600    0.42025300
 H                 -0.67852400    3.48179200   -0.55659900
 C                  0.45280700    4.50900100    0.98035200
 H                  0.58594600    4.42984500    2.06763300
 H                 -0.14120400    5.40905300    0.79084800
 C                  3.18003600   -1.57971800    1.22932200
 H                  2.12289100   -1.87761700    1.19106500
 C                  5.26323300   -0.31993600   -0.82296100
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H	5.61499700	-1.34719600	-1.01572800
C	2.57730700	-1.59262600	-1.84657600
H	1.72201300	-2.09308600	-1.37094000
O	0.34630300	0.16122200	0.01620700
H	-1.15406600	2.43147700	1.21945000
C	-2.04519100	1.91618200	2.22263400
H	-2.63838000	0.98330800	2.21586300
C	-1.16953400	1.90092100	3.48151600
H	-0.52431500	1.01072700	3.52434900
H	-1.74041900	1.93340000	4.42681500
H	-0.49840200	2.77208800	3.49523200
C	-3.04025900	3.07900700	2.25234400
H	-3.79657700	2.99099700	1.45782600
H	-2.51948600	4.03488700	2.08139000
H	-3.58484300	3.18249400	3.20688200
Li	-1.48680900	0.31314300	0.62222900
H	-0.23751100	-2.19747900	0.01061400
C	-0.81651200	-3.04722900	0.38809900
C	-2.31001500	-2.69796700	0.39474300
H	-0.65863700	-3.89021200	-0.29783400
C	-0.33442000	-3.40409700	1.80020900
N	-2.58107000	-1.56514000	1.31924600
H	-2.84563800	-3.59189500	0.77989700
C	-2.90300200	-2.43391200	-1.00874500
C	-0.66124900	-2.25664000	2.76264100
H	0.74122900	-3.61606500	1.79906900
H	-0.83641200	-4.32236900	2.13915000
C	-4.02782500	-1.24860900	1.35220300
C	-2.14639600	-1.90026300	2.69356500
C	-2.36029700	-1.20275200	-1.76335600
H	-2.65710000	-3.31234900	-1.62068000
C	-4.42398900	-2.29704700	-0.87461800
H	-0.06109900	-1.37520300	2.50401600
H	-0.40999800	-2.52614300	3.79595300
H	-4.16113200	-0.35647900	1.97367400
H	-4.57353300	-2.07312700	1.85053200
C	-4.66695900	-1.03783300	-0.03106300
H	-2.36361800	-1.03698200	3.33161100
H	-2.74518100	-2.75037400	3.07585000
N	-2.72931200	0.08710600	-1.13797900
H	-2.72652400	-1.27426400	-2.80211800
H	-1.26649000	-1.22593600	-1.81123300
H	-4.84805900	-3.17691900	-0.37372100
H	-4.90222600	-2.22936300	-1.85796900
C	-4.16906800	0.22078800	-0.77779300
H	-5.74257700	-0.90106100	0.14327500
C	-2.26432000	1.24546700	-1.93693700
C	-5.08456500	0.56777700	-1.97693600
H	-4.21735900	1.07229200	-0.08272100
H	-1.21937600	1.06160000	-2.20570100
C	-3.11472500	1.56396300	-3.17449200
H	-2.27305200	2.11909500	-1.27374800
H	-6.09862900	0.75208700	-1.59849700
H	-5.15788800	-0.28598700	-2.66239400
C	-4.57330800	1.78538200	-2.75818200
H	-2.70704900	2.45647900	-3.66569100
H	-3.05450400	0.74719200	-3.90699500

H	-4.63723400	2.68274600	-2.12557200
H	-5.20904800	1.97076200	-3.63277200
Si	3.41467800	-0.62492200	-0.41312500
C	5.51145100	0.47600800	-2.12205200
H	5.15876500	1.51038000	-2.04805500
H	6.58575400	0.51329900	-2.34822200
H	5.01128700	0.02518200	-2.98518900
C	6.13803400	0.22240600	0.32658900
H	6.10533400	-0.42466200	1.20874900
H	7.18714400	0.28736700	0.00722500
H	5.83687500	1.22552100	0.64860600
C	2.00709100	-0.69923400	-2.96603800
H	2.79183000	-0.13702600	-3.48615800
H	1.49771600	-1.31390400	-3.72148700
H	1.28291300	0.02115600	-2.57674000
C	3.47717800	-2.69137200	-2.45122500
H	3.86440300	-3.38826200	-1.69933800
H	2.91538200	-3.28556100	-3.18471800
H	4.33931200	-2.26546000	-2.97882300
C	4.02188600	-2.86731000	1.33098500
H	3.79165500	-3.40877300	2.25882000
H	3.83478600	-3.55670200	0.49993500
H	5.09768200	-2.65233400	1.34615900
C	3.34876400	-0.71403000	2.49396300
H	3.07236200	-1.28814200	3.38881000
H	4.38420000	-0.38251700	2.63271200
H	2.71742600	0.17975200	2.46619900

Structure: TS12

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 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
               25-Aug-2009
 ****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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Version=AM64L-G03RevD.01\State=1-A\HF=-1874.2024697\MP2=-
1879.5245413\RMSD=5.018e-09\Thermal=0.\PG=C01 [X(C33H61Li1N4O1Si1
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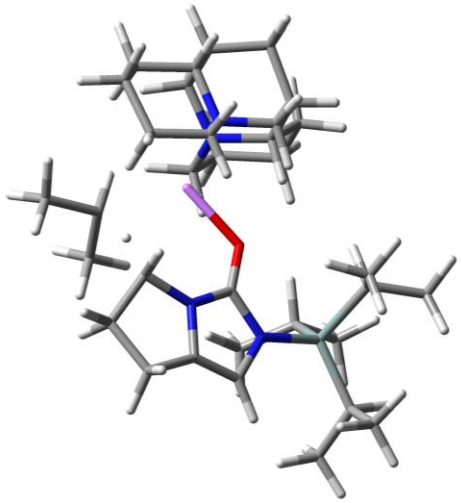

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N	0.88398500	2.50490500	-0.02205600
C	2.06686600	3.23722400	0.00559900
C	3.08933600	2.35738600	-0.09338100
H	4.15405300	2.51587000	-0.09624300
C	1.72631300	4.69147000	0.14803200
H	1.76619500	5.19503700	-0.82883800
H	2.40062900	5.23034300	0.82213500
C	-0.35030100	3.29328000	0.13215300
H	-0.74586200	3.46845500	-0.88208900
C	0.25197500	4.60916900	0.67745600
H	0.28459600	4.59224800	1.77481800
H	-0.33921000	5.48309900	0.38483800
C	2.94549800	-1.52729200	1.29323800
H	1.93135200	-1.90457400	1.09512500
C	5.26137400	-0.24107000	-0.45847700
H	5.64076800	-1.27085000	-0.56525600
C	2.69191400	-1.46203500	-1.83046800
H	1.75736300	-1.91887800	-1.47425100
O	0.30461800	0.23446500	-0.14779000
H	-1.25960700	2.49980300	0.96209800
C	-2.05136000	1.93615000	2.04355300
H	-2.66105200	1.00826000	2.04865600
C	-1.04415700	1.84351700	3.19823400
H	-0.38815500	0.96576800	3.11184500
H	-1.51217400	1.80127000	4.19820900
H	-0.38524800	2.72404300	3.20323800
C	-3.01541400	3.10547600	2.26801500
H	-3.43928200	3.14451400	3.28640800
H	-3.86350200	3.08392000	1.56922500
H	-2.50173500	4.06628300	2.10470500
Li	-1.55718800	0.44682400	0.34404300
H	-4.49368500	1.06116800	0.49917800
C	-4.95524600	0.87004300	-0.47645800
C	-4.20460900	-0.25475000	-1.19921000
H	-5.98670700	0.54237800	-0.29115100

C	-4.93829900	2.15776900	-1.30864600
N	-2.79279200	0.13779500	-1.45177700
H	-4.70441300	-0.39174100	-2.18183400
C	-4.30223700	-1.62658900	-0.49697300
C	-3.49254900	2.53402200	-1.64913400
H	-5.42848200	2.97366000	-0.76430900
H	-5.51322300	2.00155600	-2.23341700
C	-2.04030900	-0.93778400	-2.14285300
C	-2.74640700	1.35983900	-2.28646700
C	-3.66167600	-1.72519100	0.90267600
H	-5.37326700	-1.83373500	-0.36870400
C	-3.66874400	-2.68348700	-1.40903700
H	-2.96948400	2.84249600	-0.73880200
H	-3.46290800	3.38525700	-2.34112100
H	-0.98887200	-0.63459400	-2.16681300
H	-2.39032100	-1.01903600	-3.18981400
C	-2.17794800	-2.33105200	-1.49858400
H	-1.69252100	1.61763200	-2.44022700
H	-3.17750300	1.14220900	-3.28353800
N	-2.18949500	-1.58675400	0.88447800
H	-3.97947200	-2.68804100	1.33871300
H	-4.05053400	-0.94177100	1.56346400
H	-4.12852900	-2.65655000	-2.40560800
H	-3.82768300	-3.69321200	-1.01389100
C	-1.50595900	-2.46009800	-0.11260300
H	-1.66275100	-3.03213600	-2.16895800
C	-1.59279100	-1.74648000	2.23093500
C	-1.38578100	-3.93599900	0.33672700
H	-0.48757900	-2.05902000	-0.19142400
H	-2.16004100	-1.11851900	2.92564100
C	-1.50892100	-3.19474100	2.73571500
H	-0.57750800	-1.33204800	2.18140400
H	-0.79195100	-4.48105600	-0.40917200
H	-2.37230100	-4.41566400	0.35900000
C	-0.74488900	-4.05906900	1.72590400
H	-1.01242900	-3.20261100	3.71429700
H	-2.51540600	-3.60589300	2.89241800
H	0.30092000	-3.72159700	1.67914300
H	-0.72242300	-5.10859800	2.04476000
Si	3.37363300	-0.53548200	-0.29212800
C	3.85785600	-2.74962900	1.52222700
H	4.89540600	-2.45333200	1.71945600
H	3.51918400	-3.32660000	2.39356700
H	3.86848300	-3.43388500	0.66630500
C	2.85904800	-0.66572400	2.56853700
H	2.15191000	0.16181700	2.45643000
H	2.52632800	-1.27516800	3.41997800
H	3.82957300	-0.23574700	2.84210500
C	3.60760400	-2.60581900	-2.31707600
H	3.83722500	-3.33153800	-1.52860100
H	3.12738300	-3.15884500	-3.13569800
H	4.56213900	-2.22847100	-2.70369800
C	2.31640300	-0.54109700	-3.00810700
H	3.18606100	-0.00886700	-3.41067100
H	1.88979000	-1.13041800	-3.83183800
H	1.57524000	0.20811600	-2.71622400
C	5.68618500	0.51429400	-1.73542900

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 H                     6.78129000    0.56688100   -1.80298200
 H                     5.32589100    0.02114300   -2.64380900
 H                     5.30937800    1.54278300   -1.75376000
 C                     5.95972800    0.34833300    0.78465300
 H                     5.77964800   -0.25283800    1.68116800
 H                     7.04635800    0.38809400    0.62858700
 H                     5.62846100    1.36859000    1.00704500
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Structure: TS13

```
 ****************************************
 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
                27-Aug-2009
 ****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=AM64L-G03RevD.01\State=1-A\HF=-1874.2016765\MP2=-
1879.5204515\RMSD=4.805e-09\Thermal=0.\PG=C01 [X(C33H61Li1N4O1Si1)]\\@
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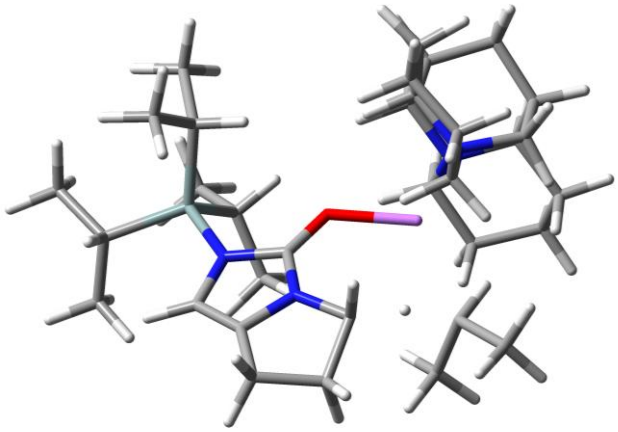

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 C                     1.23261700    1.13324400    0.08517500
 N                     2.61082700    0.92988400    0.13373500
 N                     1.03619700    2.46896300    0.11131700
 C                     2.25535600    3.13985900    0.14926400
 C                     3.23235500    2.20552300    0.17014600
 H                     4.30393400    2.31165400    0.19323400
 C                     1.99302000    4.61660300    0.12528800
 H                     2.70711800    5.17284100   -0.49143000
 H                     2.03934200    5.03434100    1.14160900
 C                    -0.15254200    3.33720600    0.01465200
 C                     0.52700200    4.65318300   -0.42866300
 H                    -0.02255600    5.53461700   -0.08222400
 H                     0.57855600    4.71184000   -1.52394700
 C                     2.78049300   -1.45592200    1.84085700
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H	1.69746300	-1.26931100	1.78414500
C	5.27852200	-0.31823400	0.20572500
H	5.39381000	0.48122200	0.95396100
C	2.80417900	-1.73047900	-1.30277300
H	1.82454900	-2.11702000	-0.98538200
O	0.34883600	0.22204300	0.04282300
H	-0.53920100	3.46544100	1.03963000
C	-2.00012400	2.21709800	-1.89916200
H	-2.55375500	1.26262200	-2.00712100
C	-3.04612500	3.33251600	-1.82382600
H	-3.82500100	3.11975500	-1.07680800
H	-3.56469500	3.52839800	-2.77866500
H	-2.57404100	4.28171700	-1.52212600
C	-1.11687800	2.38360500	-3.14227900
H	-0.38851000	1.56603400	-3.24931600
H	-0.53060600	3.31084900	-3.07176900
H	-1.68006400	2.44433100	-4.09083700
Li	-1.48924000	0.45163300	-0.46963300
H	-1.11323600	2.64259400	-0.84212900
H	-3.83160100	-3.62705000	0.97675700
C	-3.77608500	-2.57782500	1.29431900
C	-2.31672600	-2.16794900	1.53250100
C	-4.30395400	-1.65402400	0.19075900
H	-4.37725200	-2.48784600	2.20561800
C	-2.24298600	-0.72900600	2.09063800
C	-1.52415100	-2.38066400	0.22821000
H	-1.85670100	-2.82473500	2.28301300
C	-4.24944200	-0.19650500	0.69337000
C	-3.52941100	-1.96111900	-1.11050100
H	-5.35990700	-1.87705700	-0.01346300
N	-2.91129900	0.22753000	1.16174600
C	-2.75676200	-0.65096400	3.54856900
H	-1.18630300	-0.42585300	2.10314400
N	-2.07936600	-1.67679800	-0.95373600
H	-0.49158200	-2.04189000	0.35172800
H	-1.49950300	-3.46966100	0.02825300
H	-5.00826300	-0.10196400	1.48920700
H	-4.54529100	0.49840800	-0.10076300
H	-3.64795000	-3.05364700	-1.27554100
C	-4.10116200	-1.26989400	-2.35485900
C	-2.93179600	1.59837800	1.72377600
H	-2.13486800	-1.30812700	4.17107100
H	-3.78244700	-1.03516900	3.61949500
C	-2.73048000	0.78459400	4.08923300
C	-1.33387700	-2.12017100	-2.15239500
H	-4.04588900	-0.18101900	-2.24268900
H	-5.16419700	-1.53148100	-2.43902400
C	-3.34426500	-1.69382100	-3.62015100
H	-3.47432000	2.23901200	1.02208000
C	-3.50384600	1.71121400	3.14420200
H	-1.89695800	1.95853000	1.73790800
H	-1.68900400	1.13097400	4.16267300
H	-3.14658700	0.81818700	5.10371900
H	-0.27825100	-1.87946500	-1.99135300
H	-1.40954700	-3.22166100	-2.24927600
C	-1.83992300	-1.46313300	-3.43731300
H	-3.71593600	-1.14267900	-4.49204300

H	-3.53124100	-2.76027200	-3.81476500
H	-3.43251500	2.75572600	3.47272500
H	-4.57144800	1.45119800	3.15639700
H	-1.63210400	-0.38813200	-3.40669900
H	-1.27835500	-1.87243500	-4.28645600
Si	3.39877400	-0.69671000	0.19667000
C	2.57174600	-0.89353300	-2.57630900
H	2.17201600	-1.52493800	-3.38203900
H	1.85976700	-0.08095200	-2.40545800
H	3.50272200	-0.44964700	-2.94781400
C	3.69938700	-2.94784300	-1.61624700
H	3.23831700	-3.57113800	-2.39436200
H	4.68096700	-2.63996300	-1.99494600
H	3.86760900	-3.58815600	-0.74329100
C	6.14918600	-1.49757400	0.68971200
H	6.08292500	-2.35966400	0.01663900
H	7.20575800	-1.19957300	0.72732200
H	5.87111000	-1.83680700	1.69260300
C	5.82083100	0.21844700	-1.13632400
H	6.86390600	0.54552800	-1.02713100
H	5.80838200	-0.55809600	-1.90978300
H	5.24545700	1.06850500	-1.51774500
C	3.30750600	-0.69639100	3.07419200
H	3.12574000	0.38180800	2.99877000
H	2.81344900	-1.05063600	3.98925100
H	4.38563600	-0.84274000	3.21550800
C	2.97370800	-2.97607200	1.99683400
H	4.03254100	-3.26040800	2.02278300
H	2.52531000	-3.32700300	2.93660100
H	2.50073700	-3.53640200	1.18235400

Structure: TS14

```
*****************************************
 Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
               25-Aug-2009
 *****************************************
 %nosave
 %mem=10GB
 %nproc=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=AM64L-G03RevD.01\State=1-A\HF=-1874.2008291\MP2=-
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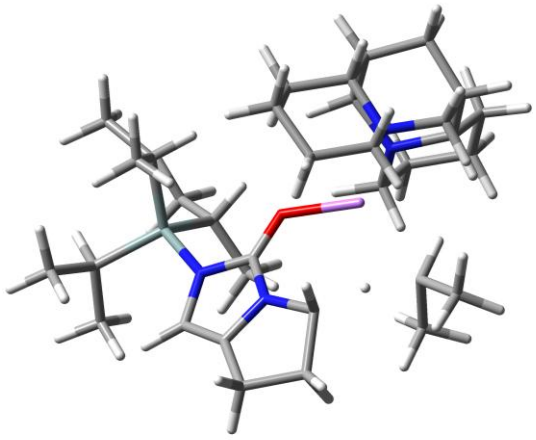

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C	1.32532300	1.03121000	-0.16289100
N	2.66733200	0.65654000	-0.22487800
N	1.28197700	2.35916200	-0.40519200
C	2.55992800	2.84962600	-0.66135100
C	3.42204300	1.81407600	-0.54919500
H	4.48906700	1.77109600	-0.68416300
C	2.45858500	4.31215900	-0.97891100
H	3.12696800	4.62645600	-1.78771700
H	2.70401800	4.91757800	-0.09421000
C	0.19303800	3.34435100	-0.54271000
C	0.93805700	4.43848600	-1.34133900
H	0.54608000	5.43872900	-1.12992700
H	0.83205200	4.26897300	-2.42114800
C	2.70030100	-1.46261800	1.89458800
H	1.63941600	-1.72818200	1.77996700
C	5.16607500	-1.06863800	-0.05885800
H	5.37974900	-2.12650800	0.16898500
C	2.42218200	-2.20607900	-1.13943700
H	1.42263000	-2.37608700	-0.71375400
O	0.34883000	0.26027800	0.08821100
H	-0.02674200	3.72530500	0.46863100
C	-2.12331600	2.24552300	-1.86717900
H	-2.79019100	1.37442600	-1.71759100
C	-2.98127200	3.50642500	-1.73062100
H	-2.33960300	4.40138900	-1.68566900
H	-3.57624600	3.50453600	-0.80510400
H	-3.68602800	3.66576100	-2.56517800
C	-1.53526000	2.13887000	-3.27987000
H	-0.96120400	1.21157400	-3.42257200
H	-0.83727400	2.96709300	-3.46810100
H	-2.29126200	2.18094600	-4.08398000
Li	-1.50857500	0.70686700	-0.21407100
H	-0.98077800	2.65841000	-1.09618000
H	-5.04523100	-1.59808900	2.31535000
C	-4.42535500	-1.81837700	1.43663500
C	-4.64896800	-0.76427600	0.34418400
C	-2.93707900	-1.74854500	1.79820900
H	-4.70407700	-2.82120700	1.09482800
C	-3.86175400	-1.13770500	-0.92902000

C	-4.29708100	0.62471800	0.91604900
H	-5.71073400	-0.72388000	0.06660900
C	-2.09741300	-2.09437600	0.54979700
C	-2.66221000	-0.37348200	2.44686800
H	-2.69888600	-2.50502400	2.55815700
N	-2.40984300	-1.24872300	-0.62418400
C	-4.44063200	-2.38256100	-1.64359800
H	-3.95043700	-0.30182800	-1.63783900
N	-2.93518500	0.73730100	1.49542800
H	-4.39151500	1.39158700	0.13913900
H	-5.04667200	0.86076300	1.69551500
H	-2.25747600	-3.16568500	0.33780800
H	-1.02944100	-1.96772900	0.75497800
H	-3.38398300	-0.29124000	3.28749300
C	-1.25961600	-0.23862200	3.05325300
C	-1.63920700	-1.64006400	-1.82528900
H	-5.48793500	-2.18200400	-1.90578600
H	-4.44756800	-3.24892600	-0.97008800
C	-3.63078800	-2.73689400	-2.89847400
C	-2.82651400	2.04286400	2.18657500
H	-0.50373900	-0.31280600	2.26390500
H	-1.09992300	-1.07328400	3.74898800
C	-1.10537900	1.10295500	3.78034600
H	-0.59242600	-1.74022800	-1.52710500
C	-2.14854200	-2.90109100	-2.53975700
H	-1.69115700	-0.79800500	-2.52831900
H	-3.73609900	-1.93308700	-3.64172000
H	-4.02599800	-3.64893200	-3.36266400
H	-3.02634200	2.82813500	1.44969500
H	-3.61108200	2.11596500	2.96543600
C	-1.45385800	2.25190500	2.82819600
H	-0.08403800	1.21671200	4.16297800
H	-1.77577800	1.12888100	4.65240000
H	-1.54454800	-3.06960000	-3.44038800
H	-2.01460300	-3.78629300	-1.90259400
H	-0.69365600	2.32213300	2.04276400
H	-1.45574900	3.21334700	3.35689900
Si	3.25608200	-1.01563200	0.11302000
C	2.21947400	-1.59604500	-2.54067900
H	1.67062000	-2.29533300	-3.18678700
H	1.65135400	-0.66207500	-2.50225500
H	3.17292400	-1.38244700	-3.03768700
C	3.11356200	-3.58137300	-1.24681500
H	2.54164600	-4.24797100	-1.90641500
H	4.12122400	-3.49942200	-1.67175700
H	3.20522100	-4.08596200	-0.27849000
C	5.94813000	-0.23587100	0.97862600
H	7.02863500	-0.39137000	0.85585700
H	5.76195300	0.83891100	0.87742500
H	5.69343900	-0.51367800	2.00618400
C	3.42562800	-2.69181600	2.48054800
H	3.01387700	-2.94723100	3.46630400
H	3.32685700	-3.58181600	1.84908900
H	4.49727300	-2.50419400	2.62042200
C	2.75929300	-0.28260500	2.88457100
H	2.35854800	-0.58454100	3.86216500
H	3.78512000	0.06578200	3.05118600

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 H                     2.17348400    0.57245000    2.53500700
 C                     5.70656600   -0.81469000   -1.48216900
 H                     6.79675900   -0.94743900   -1.50504500
 H                     5.27867700   -1.50492500   -2.21583100
 H                     5.49714500    0.20152700   -1.83376600
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N-Boc pyrrolidine (1)

Structure: TS15

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*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               23-Aug-2010
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1372.0543403\MP2=-
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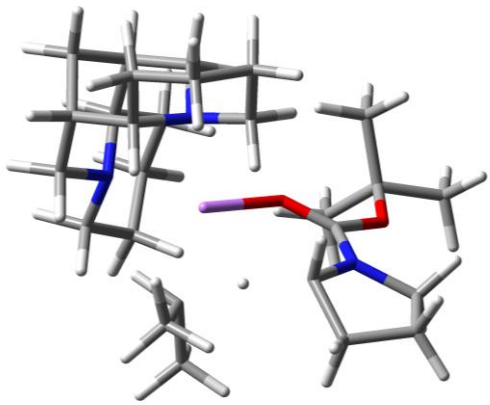

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 N                    -1.76644100    0.60909300   -1.03252800
 C                    -1.02555700    1.65413500   -1.77835200
 C                    -1.84335000    2.40025800   -2.84167000
 C                    -3.08070700    3.02760000   -2.19081900
 H                    -2.71658200    1.85621200    0.32424700
 H                    -4.33427400    1.27521800   -2.21177400
 H                    -4.73193200    2.39945600   -0.91978000
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H	-0.66592900	2.38295400	-1.04305400
H	-0.13793100	1.18255900	-2.21212700
H	-1.20943400	3.16848200	-3.30201000
H	-2.14872100	1.71982300	-3.64852000
H	-2.76005900	3.79421200	-1.47035100
H	-3.70464400	3.53626000	-2.93598900
C	-1.92764800	-0.62597700	-1.83115200
H	-0.91956400	-0.99584200	-2.04819900
H	-2.40578500	-0.42374500	-2.80507100
C	-3.85497000	0.02521100	0.21814100
C	-2.77222300	-1.71106200	-1.13323000
C	-4.13620200	-1.11168800	-0.77361800
H	-4.65755100	-0.75427100	-1.66846900
H	-4.78155300	-1.86882800	-0.30984600
H	-2.89895800	-2.52620200	-1.85852700
C	-3.20071500	-0.57911200	1.47221500
H	-3.94510000	-1.24643600	1.94824200
H	-2.96776000	0.20694600	2.19839600
N	-1.95559200	-1.33640300	1.20824500
C	-2.16534300	-2.34693800	0.13834700
H	-2.92469200	-3.07530200	0.49550500
C	-1.53448300	-1.99582600	2.46445300
H	-2.34160100	-2.66503800	2.82257800
H	-1.39919100	-1.21683300	3.22179700
C	-0.87604700	-3.13791300	-0.11399800
H	-0.09346100	-2.46151500	-0.47315000
H	-1.06556400	-3.87582700	-0.90476700
C	-0.24683800	-2.80139300	2.29222300
H	0.57992000	-2.11774300	2.06246500
H	-0.00382700	-3.29092800	3.24334200
C	-0.39668800	-3.83198600	1.16729300
H	0.55119300	-4.35385900	0.99051700
H	-1.12791600	-4.59727600	1.46613200
H	-4.79828500	0.47908600	0.54973800
Li	-0.33669300	0.22438700	0.58298700
C	-0.21126700	1.56393300	2.44451500
H	-1.08436400	0.88678000	2.43168200
C	-0.74542800	2.97498200	2.70694100
H	-1.17066400	3.11290900	3.71630200
C	0.71439200	1.09791000	3.57465700
H	1.63462700	1.69872500	3.59491900
H	0.26741100	1.17798500	4.58177200
H	1.02876300	0.05167500	3.44350300
O	1.30474200	-0.39081900	-0.22979200
C	2.43343900	0.14938000	-0.34182200
O	3.53009900	-0.50731500	-0.81427100
C	3.53957100	-1.91408800	-1.20276700
C	4.99050400	-2.12195600	-1.65302500
H	5.68174800	-1.90477400	-0.83251400
H	5.14389000	-3.15837900	-1.97220100
H	4.77211500	1.40284100	0.49736800
C	2.58363600	-2.15650600	-2.37655800
H	1.54613400	-1.99418000	-2.08295800
H	2.82402400	-1.47913000	-3.20354400
H	2.69144500	-3.18570900	-2.73782700
C	3.22890900	-2.80032000	0.00736200
H	3.92684300	-2.58250500	0.82317500

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 H                     2.21290500   -2.63281900    0.36430200
 H                     3.33966900   -3.85678700   -0.26319800
 N                     2.72173200    1.41667200   -0.05408300
 C                     4.09912400    1.95894200   -0.16683200
 H                     5.23245000   -1.46005500   -2.49075000
 C                     1.74469100    2.39666500    0.48346900
 C                     2.68294000    3.40179800    1.15851400
 H                     2.96072600    3.07098100    2.16984200
 H                     2.22245600    4.39105300    1.25679200
 H                     0.05683500    3.72089000    2.60059100
 H                     1.28658900    2.89994500   -0.38780100
 H                     0.69193800    1.82561200    1.36211700
 H                    -1.52886100    3.25649800    1.98678500
 H                     4.48018900    1.84635400   -1.18722000
 C                     3.94393100    3.42467900    0.26597600
 H                     3.76491800    4.05732800   -0.61239000
 H                     4.84690100    3.79568200    0.76584600
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Structure: TS16

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               23-Aug-2010
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1372.0579048\MP2=-
1376.5137643\RMSD=4.586e-09\PG=C01 [X(C27H50Li1N3O2)]\\@
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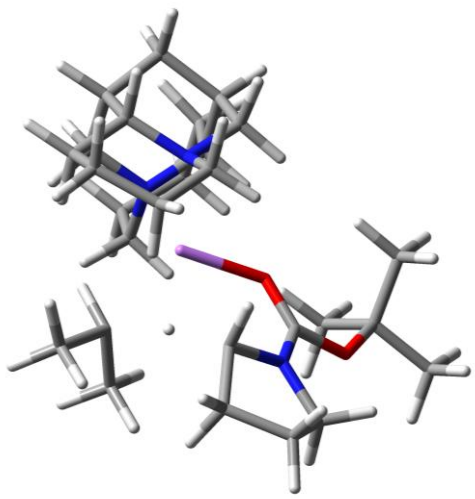

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0 1
 C                    -2.05352400   -3.55665700    0.01100900
 C                    -1.58275900   -2.12086300   -0.32679200
 N                    -1.73909000   -1.15808800    0.80032800
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C	-1.14956100	-1.69445900	2.04840600
C	-1.63632400	-3.09578400	2.44689500
C	-1.40030500	-4.08180700	1.29681900
H	-0.50257600	-2.16948000	-0.51184700
H	-3.14399600	-3.59011300	0.12918400
H	-1.81277500	-4.21196300	-0.83678400
H	-0.06262400	-1.72671200	1.90136300
H	-1.33971200	-0.97020800	2.84682900
H	-1.10331200	-3.41358200	3.35188900
H	-2.70403100	-3.07302700	2.70468900
H	-0.31875900	-4.20045300	1.13762600
H	-1.79208200	-5.07601300	1.54522600
C	-3.12221500	-0.67696500	1.00047300
H	-3.07975400	0.12262200	1.74893300
H	-3.77578600	-1.46144800	1.41968400
C	-2.26129300	-1.57642300	-1.60470800
C	-3.78831000	-0.17456100	-0.29552000
C	-3.74629300	-1.29219400	-1.34385800
H	-4.27533400	-2.18455300	-0.99157600
H	-4.24292900	-0.97165900	-2.26888600
H	-4.83029200	0.06419600	-0.04292200
C	-1.61068800	-0.30202700	-2.17807800
H	-2.05691700	-0.12299200	-3.17515900
H	-0.53579900	-0.45534500	-2.32338100
N	-1.77428000	0.90947000	-1.33795000
C	-3.18896100	1.10298600	-0.92068500
H	-3.79176400	1.29338900	-1.83422000
C	-1.31716300	2.08628300	-2.11169700
H	-1.91174300	2.16792400	-3.04299900
H	-0.27746200	1.90847400	-2.40708600
C	-3.32073400	2.34984600	-0.03775300
H	-2.72644200	2.22507400	0.87462000
H	-4.36995700	2.45490800	0.26845800
C	-1.42689400	3.38802400	-1.31564000
H	-0.72399700	3.35741100	-0.47702800
H	-1.12141000	4.22117700	-1.96125000
C	-2.85024300	3.60136400	-0.78887100
H	-2.88948800	4.48018600	-0.13438500
H	-3.53285300	3.79918300	-1.62842000
H	-2.15380700	-2.35004800	-2.37700400
Li	-0.33384000	0.50923500	0.31218300
C	-0.04398900	1.78628900	2.19241900
H	-0.98621900	1.20466700	2.26024500
C	-0.38400200	3.23443000	2.56121900
H	-0.68360100	3.36485000	3.61628200
C	0.94749600	1.19309300	3.20238600
H	1.91790700	1.70686400	3.13895500
H	0.61966000	1.27910100	4.25421400
H	1.14756300	0.12891800	3.01360300
O	1.23255700	-0.47474600	-0.31283800
C	2.41741800	-0.05870700	-0.30933700
O	3.49904900	-0.87155300	-0.45423700
C	3.40412400	-2.30614700	-0.71450200
C	4.87428200	-2.71156800	-0.86992600
H	5.43558300	-2.47540200	0.03967100
H	4.95289600	-3.78767700	-1.05796500
H	4.69971300	1.31761200	0.69766300

C	2.64102500	-2.56912500	-2.01809200
H	1.59434600	-2.27492000	-1.92997000
H	3.09542800	-2.00684700	-2.84144900
H	2.68933000	-3.63527800	-2.26746100
C	2.77979700	-3.02383700	0.48661600
H	3.34002300	-2.79253300	1.39910200
H	1.74249400	-2.71817000	0.62717400
H	2.81183700	-4.10863400	0.33199200
N	2.77330400	1.21729600	-0.18733500
C	4.18166600	1.67239700	-0.20271300
H	5.33530700	-2.17755900	-1.70710100
C	1.79300900	2.31637600	-0.00345100
C	2.70176100	3.45425700	0.47385400
H	2.84427300	3.41508900	1.56334100
H	2.28431700	4.43948300	0.23898900
H	0.48101400	3.89478200	2.40020600
H	1.40586800	2.57178300	-1.00610000
H	0.76430700	1.97062200	0.98545900
H	-1.20116200	3.63853500	1.94717900
H	4.71260700	1.26606200	-1.06910800
C	4.05566500	3.20230000	-0.22426400
H	4.01215100	3.55731900	-1.26162200
H	4.91119400	3.68722500	0.26062800

Structure: TS17

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               23-Aug-2010
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1372.0530505\MP2=-
1376.5061768\RMSD=4.518e-09\PG=C01 [X(C27H50Li1N3O2)]\\@
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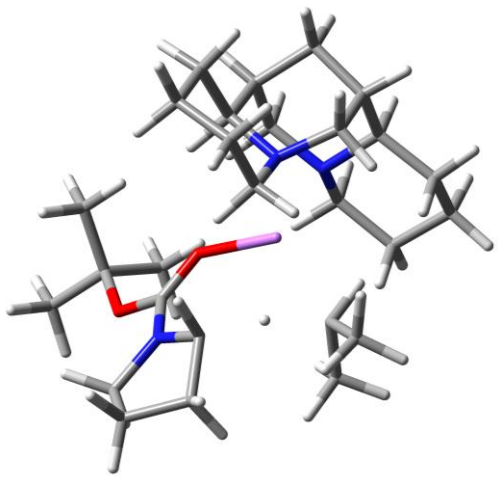

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0 1
 C                  2.01828800    1.55480200   -3.18345200
 C                  1.57493100    0.65073100   -2.00780000
 N                  1.77794800    1.25987300   -0.66132000
 C                  1.24844600    2.64437500   -0.60433200
 C                  1.73649200    3.57557000   -1.72301400
 C                  1.41013900    2.95957900   -3.08815500
 H                  0.48786000    0.51454600   -2.10164500
 H                  3.11151000    1.64568300   -3.21090500
 H                  1.72256300    1.07014500   -4.12342800
 H                  0.15693600    2.57890100   -0.65822100
 H                  1.48684600    3.04938200    0.38407700
 H                  1.25066700    4.55251800   -1.60670000
 H                  2.81795800    3.75204800   -1.64206000
 H                  0.31825000    2.89753200   -3.20584000
 H                  1.78007000    3.59137400   -3.90514000
 C                  3.16755200    1.19277000   -0.15497600
 H                  3.13914700    1.50439300    0.89509400
 H                  3.82347700    1.91127400   -0.67553800
 C                  2.23891200   -0.74401000   -2.08200700
 C                  3.82170700   -0.19547800   -0.29208900
 C                  3.73508000   -0.64382000   -1.75537700
 H                  4.25144000    0.06132400   -2.41574700
 H                  4.22099100   -1.61899600   -1.88861700
 H                  4.87310200   -0.07823700    0.00347200
 C                  1.60783700   -1.80558800   -1.15969100
 H                  2.04821600   -2.78423700   -1.43332600
 H                  0.53047100   -1.86900800   -1.33430400
 N                  1.80669000   -1.56379500    0.29013300
 C                  3.23946000   -1.31576800    0.59655600
 H                  3.80992400   -2.23160400    0.32966400
 C                  1.32933200   -2.75122900    1.03308600
 H                  1.87315800   -3.65068900    0.68153300
 H                  0.27309200   -2.89629200    0.78655800
 C                  3.45504300   -1.09334700    2.09903500
 H                  2.92766200   -0.18998400    2.42655800
 H                  4.52557100   -0.92513100    2.27549500
 C                  1.50466100   -2.61335100    2.54630600
 H                  0.85069700   -1.81865700    2.91999800
 H                  1.17893300   -3.54617500    3.02345400
 C                  2.95994500   -2.29765800    2.90966100
 H                  3.05491700   -2.10272200    3.98444400
 H                  3.59314300   -3.16942700    2.68780400
 H                  2.09904000   -1.10736500   -3.10896400
 Li                 0.32112000    0.17949700    0.58121500
 C                 -0.00248800    1.03092500    2.67145700
 H                  0.93140200    0.44797000    2.54364400
 C                 -0.90459900    0.24941000    3.63546300
 H                 -0.46622100    0.09959500    4.63831800
 C                  0.39592400    2.38425000    3.26732000
 H                 -0.46027500    3.07630400    3.26868100
 H                  0.75449000    2.32586800    4.30995900
 H                  1.19074300    2.87245700    2.68449000
 O                 -1.24371600   -0.51022700   -0.33711300
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C	-2.45956400	-0.21544800	-0.21309900
O	-3.47105000	-1.02926800	-0.62768100
C	-3.27156900	-2.23963300	-1.42008000
C	-2.53203900	-3.30148900	-0.60039800
H	-3.05171000	-3.47604500	0.34793400
H	-2.50131400	-4.24767400	-1.15300900
H	-1.51137400	-2.98574800	-0.38560700
C	-2.55502600	-1.90735800	-2.73387200
H	-3.10830800	-1.13680200	-3.28217000
H	-1.54273900	-1.54481800	-2.54905900
H	-2.50035200	-2.80154900	-3.36523100
C	-4.70931000	-2.69333700	-1.69847200
H	-5.24066400	-2.88108700	-0.75998700
H	-5.25535700	-1.92471200	-2.25475800
H	-4.70898300	-3.61616500	-2.28842700
N	-2.92787100	0.91334900	0.31138900
C	-2.06314600	1.98258800	0.87262800
H	-0.91823500	1.43131800	1.63836400
H	-1.75462100	2.61777000	0.02202200
C	-4.37741000	1.20170600	0.42754100
C	-4.41076600	2.64395300	0.95205400
H	-5.29991600	2.83072500	1.56620000
C	-3.07188300	2.77457100	1.71074300
H	-2.76380600	3.81771600	1.84254400
H	-4.43220500	3.34653600	0.10937600
H	-1.85479000	0.77932400	3.78927300
H	-4.87742600	1.07732200	-0.53805000
H	-4.84233900	0.49955300	1.13137700
H	-1.16696500	-0.74477500	3.24429300
H	-3.18299000	2.34149900	2.71518800

Structure: TS18

```
 ****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               23-Aug-2010
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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Version=EM64L-G09RevA.01\State=1-A\HF=-1372.0550332\MP2=-
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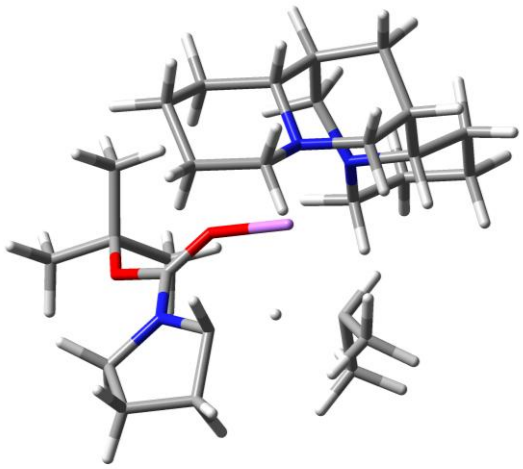

0 1

C	4.36072100	1.01433800	-1.50674700
C	3.24449500	0.11423700	-0.92574800
N	2.03738300	0.86468400	-0.48349800
C	1.55878600	1.78402100	-1.54073000
C	2.62630800	2.72773100	-2.11547900
C	3.82399800	1.91743700	-2.62564100
H	2.90630800	-0.52731900	-1.75105800
H	4.80408400	1.64351500	-0.72467400
H	5.16679400	0.37177600	-1.88493700
H	1.16532800	1.16312000	-2.35608700
H	0.71424900	2.34550800	-1.13105300
H	2.17972800	3.31875300	-2.92505700
H	2.95978200	3.44380800	-1.35174100
H	3.50627400	1.29730500	-3.47658000
H	4.61638900	2.57927400	-2.99630300
C	2.19401200	1.54532900	0.82104200
H	1.20502800	1.92155000	1.10375500
H	2.85805400	2.42384400	0.74803100
C	3.75260300	-0.80111300	0.20803100
C	2.76524600	0.63617700	1.92951400
C	4.09044000	0.03191100	1.45118600
H	4.82555300	0.81271900	1.22756800
H	4.52769800	-0.60279500	2.23275300
H	2.93841700	1.27706600	2.80448300
C	2.76723900	-1.91803000	0.61125400
H	3.31352200	-2.61264500	1.27757300
H	2.46239600	-2.49373400	-0.26972300
N	1.53328900	-1.45261100	1.29396700
C	1.85494000	-0.51648600	2.40467300
H	2.45252800	-1.07163500	3.15921300
C	0.80951600	-2.63558800	1.81736100
H	1.47933500	-3.21197700	2.48542200
H	0.56586200	-3.28134900	0.96650700
C	0.57774400	-0.05265600	3.11590400
H	-0.07013500	0.48041100	2.41104600
H	0.85628600	0.65159200	3.91096300

C	-0.46425400	-2.26037800	2.57860700
H	-1.18871500	-1.82825900	1.88188000
H	-0.91403600	-3.17730100	2.97957000
C	-0.17773600	-1.25360400	3.69592800
H	-1.11229300	-0.93106700	4.17073900
H	0.43134800	-1.72554600	4.48103400
H	4.65253100	-1.30657200	-0.16676500
Li	0.29865300	-0.53092000	-0.32663400
C	0.16591300	-1.77720200	-2.26939800
H	1.16679600	-1.33445600	-2.10631300
C	-0.40075600	-1.16388400	-3.55576200
H	0.19053400	-1.39577600	-4.45951300
C	0.35747200	-3.28922300	-2.42273200
H	-0.61641800	-3.80229900	-2.44550900
H	0.88841200	-3.58410600	-3.34472400
H	0.91616000	-3.72370600	-1.57973800
O	-1.17871600	0.61137900	0.11623200
C	-2.41480300	0.41471300	0.02923600
O	-3.33795600	1.37566800	0.31326900
C	-3.00562300	2.78923500	0.48036500
C	-2.36951700	3.33294700	-0.80321900
H	-3.03554600	3.16838900	-1.65727800
H	-2.19558600	4.41091100	-0.70858300
H	-1.41687000	2.84083500	-1.00537800
C	-2.11632900	3.00456800	1.71031800
H	-2.56521200	2.52784700	2.58860500
H	-1.12122300	2.58692000	1.55685300
H	-2.02338800	4.07734400	1.91612100
C	-4.38138300	3.42655100	0.70594700
H	-5.03803200	3.23575900	-0.14875300
H	-4.85457800	3.01300000	1.60242900
H	-4.28112500	4.50969200	0.83381000
N	-2.99724200	-0.73683900	-0.30214300
C	-2.25902000	-1.96365700	-0.70495200
H	-0.95803400	-1.73515500	-1.37173400
H	-2.11791100	-2.57326900	0.20524500
C	-4.46945900	-0.86213400	-0.44768900
C	-4.66195000	-2.31779300	-0.89835900
H	-5.53463200	-2.42495900	-1.55393000
C	-3.31360500	-2.66444500	-1.56775100
H	-3.14153000	-3.74467500	-1.62852700
H	-4.81922300	-2.96288900	-0.02497300
H	-1.41719400	-1.53575200	-3.74663100
H	-4.97641800	-0.62921400	0.49469600
H	-4.82970900	-0.14860600	-1.19884500
H	-0.47839900	-0.06830900	-3.49290200
H	-3.30975900	-2.27582000	-2.59632300

N-Boc piperidine (11)

Structure: TS19

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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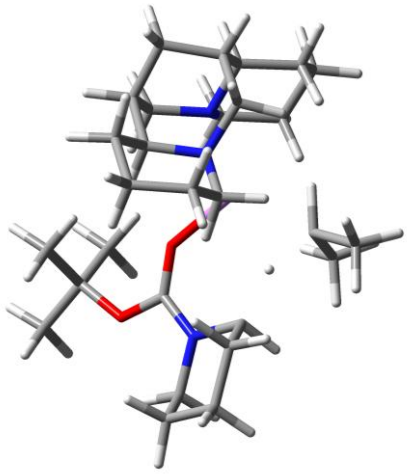

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 C                -1.28953000   -0.83614700   -2.02601500
 N                -1.52711200   -1.43357100   -0.68228300
 C                -0.71594900   -2.65752200   -0.47910600
 C                -0.83646800   -3.70911200   -1.59104200
 C                -0.49611800   -3.07891300   -2.94649100
 H                -0.25013300   -0.47757000   -2.00278800
 H                -2.41993500   -2.18627700   -3.32868100
 H                -1.09342000   -1.34402100   -4.11946400
 H                 0.33045100   -2.34365600   -0.39996700
 H                -0.98720600   -3.07633800    0.49435700
 H                -0.15959800   -4.54240900   -1.36507300
 H                -1.85176500   -4.12841000   -1.62043600
 H                 0.56108300   -2.77492200   -2.94947400
 H                -0.61720800   -3.80479900   -3.76008100
 C                -2.95009600   -1.65458500   -0.34394600
 H                -2.98613400   -1.92479400    0.71720200
 H                -3.37239700   -2.50959100   -0.89923700
 C                -2.21258400    0.38383300   -2.24756500
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C	-3.85637100	-0.44000900	-0.62591400
C	-3.68396100	-0.02245200	-2.09076300
H	-3.95556800	-0.83900400	-2.76849800
H	-4.34132800	0.82317500	-2.33040400
H	-4.88922700	-0.76855900	-0.44810000
C	-1.93116700	1.57499700	-1.31033600
H	-2.52504600	2.43390300	-1.67986600
H	-0.87717000	1.86056800	-1.36430600
N	-2.25004400	1.33111300	0.11629200
C	-3.63028300	0.80059300	0.26578800
H	-4.33524300	1.57128600	-0.11434300
C	-2.11356000	2.60722600	0.85236000
H	-2.77870400	3.36975200	0.39979800
H	-1.08526700	2.95979600	0.72224300
C	-3.98591400	0.57969200	1.74159800
H	-3.33894300	-0.19137600	2.17553600
H	-5.01676400	0.20600500	1.79760400
C	-2.44127400	2.46784300	2.33940500
H	-1.69712100	1.82357500	2.81870500
H	-2.36185700	3.45523400	2.81129700
C	-3.84133200	1.87920600	2.54372500
H	-4.03149000	1.69687600	3.60799700
H	-4.59819500	2.60185400	2.20460700
H	-2.02583500	0.74413800	-3.26817700
Li	-0.48078700	-0.09267400	0.66414800
C	-0.27614500	-0.86188900	2.76049700
H	-1.30295600	-0.53643300	2.49660900
C	0.27836000	0.13486500	3.78601400
H	-0.31360400	0.19748700	4.71597400
C	-0.39833100	-2.25568700	3.38464200
H	0.59821400	-2.68930900	3.55994200
H	-0.91710800	-2.26326800	4.35933600
H	-0.93604700	-2.95902400	2.73258400
O	1.05752900	0.81842900	-0.04975900
C	2.29869600	0.75756200	0.10038300
O	3.13761900	1.67558900	-0.45499500
C	2.70311500	2.77187700	-1.31543500
C	1.78663700	3.73067800	-0.54818200
H	2.28124400	4.07196800	0.36769800
H	1.56604700	4.60954500	-1.16484000
H	0.84952200	3.24553800	-0.27635800
C	2.05596600	2.22395300	-2.59236700
H	2.74411600	1.53856100	-3.09938800
H	1.13283900	1.68778200	-2.36971000
H	1.82811300	3.04705300	-3.27930800
C	4.02584500	3.47001800	-1.65394300
H	4.51703800	3.82533700	-0.74242500
H	4.70595600	2.78189300	-2.16622400
H	3.84335700	4.32950200	-2.30789200
N	2.95975500	-0.17739200	0.79767700
C	4.43123300	-0.23338000	0.85105500
H	4.86624700	0.62467900	0.34104400
H	4.71974700	-0.18128600	1.91046300
C	2.25964100	-1.28350600	1.49666500
C	2.73055400	-2.60938200	0.88243500
H	2.38433300	-2.69495200	-0.16062600
C	4.93631700	-1.54961900	0.24152900

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 H                     6.02856500   -1.59734000    0.34812800
 H                     2.26824500   -3.44176100    1.43052700
 H                     1.29628500   -0.15363400    4.08490200
 H                     2.66680000   -1.25515500    2.52322500
 H                     0.84602000   -1.03737000    1.87040300
 H                     0.35620100    1.15437400    3.38005400
 C                     4.26493400   -2.76768900    0.89184400
 H                     4.72094100   -1.53903700   -0.83696200
 H                     4.60718500   -2.85223800    1.93406100
 H                     4.58111500   -3.68869100    0.38034300
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Structure: TS20

```
 ****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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Version=EM64L-G09RevA.01\State=1-A\HF=-1411.0887773\MP2=-
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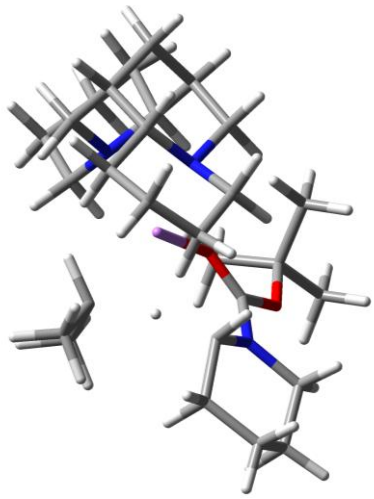

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 C                     3.07708900    2.94394200   -0.01558400
 C                     2.22246600    1.69313200   -0.33204300
 N                     2.15276300    0.71285600    0.78640800
 C                     1.77823000    1.37717600    2.05598400
 C                     2.64200400    2.58924600    2.43426600
 C                     2.64010200    3.61458300    1.29405600
 H                     1.19009900    2.03706500   -0.47172000
 H                     4.13947100    2.67980900    0.05916400
 H                     2.99090400    3.64761900   -0.85450000
 H                     0.73595400    1.70317900    1.95209800
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H	1.79443000	0.62039300	2.84632700
H	2.24924400	3.03082000	3.35891200
H	3.67232500	2.27575000	2.65148900
H	1.62551800	4.02275500	1.17649700
H	3.29554600	4.46312400	1.52641100
C	3.35800700	-0.12819700	0.93327600
H	3.12635200	-0.89537500	1.68085800
H	4.21565100	0.44354500	1.32873700
C	2.67917900	1.00057200	-1.63611400
C	3.81641000	-0.77665000	-0.38746300
C	4.04049000	0.32217800	-1.43240000
H	4.80370700	1.03431100	-1.10001400
H	4.39750800	-0.11089900	-2.37585200
H	4.76327300	-1.29107700	-0.17483700
C	1.68807700	-0.04343600	-2.18721500
H	2.03103300	-0.32061800	-3.20248200
H	0.68989700	0.39712500	-2.29250100
N	1.54847300	-1.26689000	-1.36011300
C	2.87331500	-1.83729000	-0.99376900
H	3.37093800	-2.16952100	-1.92954600
C	0.77354800	-2.26958700	-2.12668400
H	1.30020500	-2.49558400	-3.07468400
H	-0.18900800	-1.81878700	-2.39104500
C	2.69473100	-3.08609800	-0.12197000
H	2.18247600	-2.82126300	0.81001500
H	3.68671500	-3.47100200	0.14896800
C	0.55512800	-3.56321300	-1.34020500
H	-0.08406800	-3.35458300	-0.47635900
H	0.01488100	-4.27516200	-1.97686500
C	1.88523300	-4.15668300	-0.86387600
H	1.70856800	-5.02316100	-0.21568700
H	2.46428500	-4.51765900	-1.72673100
H	2.75749800	1.78292200	-2.40324100
Li	0.29989300	-0.53486600	0.33876900
C	-0.23828600	-1.65542100	2.21270400
H	0.82424600	-1.33161300	2.20672900
C	-0.23051600	-3.12780400	2.64388000
H	0.21968300	-3.29384200	3.64004100
C	-0.96765800	-0.79891300	3.25674400
H	-2.02761300	-1.08459600	3.31958900
H	-0.56086000	-0.89468300	4.28034100
H	-0.95063700	0.26977300	3.00105000
O	-0.97374700	0.85947300	-0.07303900
C	-2.20694100	0.77462600	-0.25216200
O	-2.97186100	1.85891600	-0.54078600
C	-2.44774000	3.21835700	-0.66556200
C	-3.71479200	4.03079700	-0.95808000
H	-4.43040300	3.93741600	-0.13498200
H	-3.46505200	5.08969700	-1.08306300
H	-4.72341900	0.58445400	-0.73765700
C	-1.47833000	3.30882200	-1.84912400
H	-0.57933600	2.71820700	-1.66987800
H	-1.96222800	2.94437100	-2.76209900
H	-1.18682800	4.35262700	-2.01227700
C	-1.81803300	3.67960600	0.65305000
H	-2.52752500	3.54645500	1.47696000
H	-0.91281600	3.11583100	0.87978600

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 H                    -1.56630500    4.74466600    0.58999700
 N                    -2.92096100   -0.36577100   -0.19939900
 C                    -4.28664800   -0.41252300   -0.76294200
 H                    -4.19607300    3.67647100   -1.87531800
 C                    -2.20969900   -1.64895300    0.03279100
 C                    -3.14859500   -2.66078700    0.69736200
 H                    -3.29283300   -2.38767300    1.75369800
 H                    -2.64287200   -3.63473000    0.70160200
 H                    -1.25075200   -3.53003100    2.69947100
 H                    -1.93235200   -2.03934800   -0.96439900
 H                    -1.12215200   -1.58214700    1.00163800
 H                     0.31930700   -3.76821500    1.93884300
 C                    -4.53332100   -2.78886900    0.04625300
 H                    -4.43154800   -3.19368700   -0.97232800
 H                    -5.17276100   -3.48624100    0.60531300
 H                    -4.21046700   -0.72000200   -1.81946000
 C                    -5.18196600   -1.40500300   -0.01922100
 H                    -6.15541300   -1.43863300   -0.52616600
 H                    -5.36203400   -1.03379300    0.99946100
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Structure: TS21

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 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
                22-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1411.0856645\MP2=-
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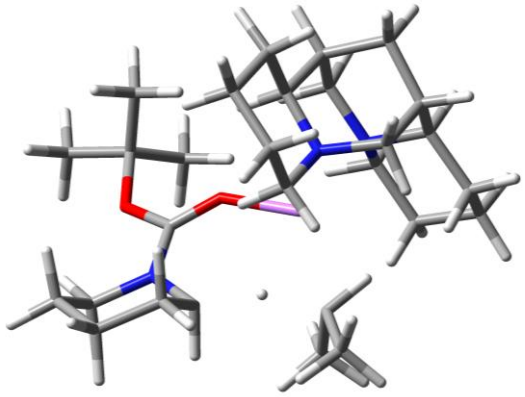

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0 1
 C                    -1.38411500   -1.85162900   -3.18970200
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N	-1.52715300	-1.43355500	-0.68216300
C	-0.71590000	-2.65741200	-0.47885200
C	-0.83630400	-3.70912100	-1.59069000
C	-0.49600300	-3.07900500	-2.94619500
H	-0.25024600	-0.47756800	-2.00275300
H	-2.41990700	-2.18658000	-3.32847800
H	-1.09345700	-1.34430300	-4.11934700
H	0.33046500	-2.34344300	-0.39969500
H	-0.98716100	-3.07616700	0.49463500
H	-0.15936800	-4.54234000	-1.36463700
H	-1.85156800	-4.12850400	-1.62006200
H	0.56116700	-2.77490800	-2.94919600
H	-0.61701100	-3.80497600	-3.75972200
C	-2.95011400	-1.65461500	-0.34379200
H	-2.98611600	-1.92472900	0.71738100
H	-3.37239000	-2.50968700	-0.89900100
C	-2.21274200	0.38367900	-2.24760100
C	-3.85643500	-0.44009300	-0.62582600
C	-3.68409500	-0.02265500	-2.09071900
H	-3.95568200	-0.83928500	-2.76837000
H	-4.34150600	0.82292100	-2.33041900
H	-4.88927600	-0.76865300	-0.44794700
C	-1.93135600	1.57494600	-1.31049200
H	-2.52530900	2.43378400	-1.68006000
H	-0.87737700	1.86057600	-1.36455800
N	-2.25013500	1.33115700	0.11617300
C	-3.63034100	0.80057400	0.26578900
H	-4.33536000	1.57121800	-0.11432600
C	-2.11369500	2.60733000	0.85214400
H	-2.77898000	3.36975900	0.39962700
H	-1.08545800	2.96000800	0.72188000
C	-3.98583100	0.57971700	1.74163800
H	-3.33880900	-0.19133100	2.17553500
H	-5.01666900	0.20601300	1.79775400
C	-2.44120900	2.46797200	2.33923400
H	-1.69695300	1.82375800	2.81845100
H	-2.36179600	3.45537600	2.81109800
C	-3.84120600	1.87925000	2.54373600
H	-4.03121500	1.69691300	3.60803300
H	-4.59815000	2.60185800	2.20471900
H	-2.02603300	0.74389200	-3.26825200
Li	-0.48085900	-0.09252000	0.66417200
C	-0.27611400	-0.86189500	2.76040800
H	-1.30299400	-0.53659500	2.49659400
C	0.27831200	0.13488200	3.78595100
H	-0.31372900	0.19752900	4.71586300
C	-0.39810200	-2.25571200	3.38454900
H	0.59851400	-2.68902500	3.56021100
H	-0.91721500	-2.26342500	4.35906000
H	-0.93536900	-2.95923900	2.73232700
O	1.05752500	0.81828900	-0.04993300
C	2.29868100	0.75757300	0.10040800
O	3.13757100	1.67574900	-0.45476900
C	2.70307400	2.77186900	-1.31542800
C	1.78644800	3.73069200	-0.54837800
H	2.28084000	4.07191000	0.36764500

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 H                    1.56606200    4.60960000   -1.16505100
 H                    0.84923500    3.24559300   -0.27681100
 C                    2.05607600    2.22374500   -2.59234700
 H                    2.74438000    1.53848500   -3.09933800
 H                    1.13306100    1.68738700   -2.36967400
 H                    1.82805500    3.04677100   -3.27932200
 C                    4.02578600    3.47006400   -1.65389300
 H                    4.51686600    3.82552900   -0.74237000
 H                    4.70599600    2.78192500   -2.16602200
 H                    3.84330100    4.32945600   -2.30796300
 N                    2.95974900   -0.17733400    0.79775300
 C                    4.43122400   -0.23323700    0.85125700
 H                    4.86622600    0.62494500    0.34144500
 H                    4.71963800   -0.18131900    1.91069900
 C                    2.25964600   -1.28360500    1.49649600
 C                    2.73066800   -2.60933800    0.88202500
 H                    2.38455100   -2.69467400   -0.16109300
 C                    4.93643900   -1.54933800    0.24153000
 H                    6.02867900   -1.59702300    0.34822200
 H                    2.26835000   -3.44187100    1.42987300
 H                    1.29620800   -0.15363000    4.08493200
 H                    2.66677800   -1.25541500    2.52307100
 H                    0.84604400   -1.03739500    1.87019000
 H                    0.35619200    1.15438800    3.37999100
 C                    4.26505500   -2.76755700    0.89156400
 H                    4.72116100   -1.53857000   -0.83697900
 H                    4.60720000   -2.85225800    1.93380300
 H                    4.58133900   -3.68845700    0.37994400
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Structure: TS22

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 ******************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               21-Feb-2011
 ******************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1411.0881322\MP2=-
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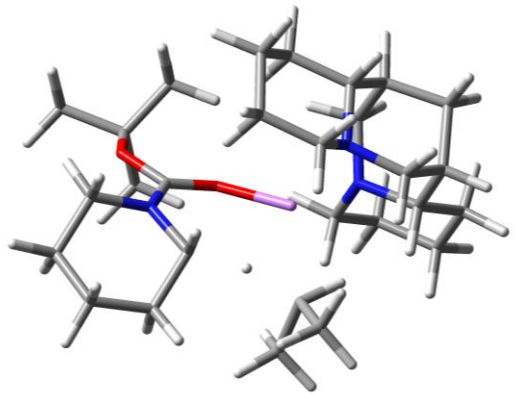

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N	2.27009700	0.64781900	-0.61080300
C	1.89945300	1.36645500	-1.85180700
C	3.05724800	2.10125300	-2.54422500
C	4.20761700	1.12542100	-2.82351500
H	3.05926200	-1.02983900	-1.53956000
H	5.09220800	1.15546500	-0.85686600
H	5.39355200	-0.33978200	-1.73319100
H	1.49215500	0.62027100	-2.54659700
H	1.08132200	2.05027200	-1.60620700
H	2.68925800	2.54878000	-3.47614600
H	3.41609900	2.93036500	-1.91899600
H	3.87732500	0.37636400	-3.55779400
H	5.06372400	1.64680700	-3.26918800
C	2.45067600	1.56296300	0.53632400
H	1.49550200	2.07467200	0.69128800
H	3.19642800	2.34857600	0.32393700
C	3.81520100	-0.97346400	0.47520000
C	2.89794800	0.85064100	1.82953500
C	4.18106500	0.06062000	1.54827800
H	4.98971600	0.72166000	1.21797500
H	4.53141500	-0.44045400	2.45997000
H	3.09480500	1.63679700	2.57102500
C	2.72805600	-1.90882900	1.04387200
H	3.19289000	-2.49004200	1.86301100
H	2.40697600	-2.62827500	0.28325100
N	1.51406300	-1.22471100	1.55635200
C	1.87043300	-0.10715700	2.47056100
H	2.38149200	-0.53784600	3.35779300
C	0.68019200	-2.21937100	2.27188900
H	1.27446700	-2.67988000	3.08541300
H	0.42620300	-3.01387500	1.56262500
C	0.60576000	0.58921200	2.98773200
H	0.04598500	1.01436300	2.14662500
H	0.90330000	1.42190700	3.63873100
C	-0.59468600	-1.60735900	2.85648600
H	-1.25520700	-1.29745700	2.04077100

H	-1.12751100	-2.38346400	3.42008500
C	-0.28265200	-0.40182700	3.74947900
H	-1.21001100	0.08310400	4.07776300
H	0.24010400	-0.73423300	4.65840600
H	4.68120500	-1.61057800	0.25120500
Li	0.41530600	-0.55440400	-0.27982700
C	0.23376200	-2.18959600	-1.83429200
H	1.26165100	-1.79831600	-1.70056800
C	-0.18145800	-1.84302000	-3.27046600
H	0.49029800	-2.26259400	-4.04130600
C	0.32323200	-3.70884900	-1.64615800
H	-0.67271600	-4.17209100	-1.69785600
H	0.94210200	-4.21808600	-2.40655500
H	0.73820500	-3.98175100	-0.66405200
O	-0.98497500	0.75145600	-0.32632700
C	-2.19157400	0.63154800	-0.02601800
O	-2.97728500	1.71003900	0.24078900
C	-2.58324400	3.08864000	-0.05329200
C	-2.26911200	3.24291600	-1.54554700
H	-3.12059700	2.90998200	-2.14894300
H	-2.07923300	4.29718700	-1.77700100
H	-1.39181900	2.65836900	-1.82770600
C	-1.41566100	3.52797900	0.83567400
H	-1.64664800	3.33632900	1.88926700
H	-0.50270400	2.99426100	0.57230000
H	-1.24319300	4.60376400	0.71540000
C	-3.84843700	3.87476000	0.30953500
H	-4.69802200	3.53540800	-0.29138400
H	-4.09776700	3.73773100	1.36690300
H	-3.69596600	4.94339000	0.12456500
N	-2.84937400	-0.53425600	0.09801100
C	-2.26827600	-1.80878300	-0.40210300
H	-0.92258200	-1.82709800	-1.01439000
H	-2.26863100	-2.50248300	0.45788600
C	-4.23094200	-0.60185800	0.60866100
C	-5.18915600	-1.14514000	-0.45717300
H	-5.25610600	-0.41510700	-1.27637100
C	-3.22789200	-2.37380200	-1.46277100
H	-2.86213600	-3.35977600	-1.77653600
H	-6.19461700	-1.23586400	-0.02425000
H	-1.18430100	-2.23085900	-3.49169900
H	-4.21673600	-1.28826000	1.46805500
H	-4.54953300	0.37693300	0.96517200
H	-0.22594900	-0.75644200	-3.43620300
C	-4.69140200	-2.49139900	-0.99701700
H	-5.34287400	-2.83766300	-1.81217300
H	-4.75746500	-3.24497400	-0.19736500
H	-3.19692300	-1.73593900	-2.35943900

N-Boc Indoline (78)

Structure: TS23

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               14-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1982.4126535\MP2=-
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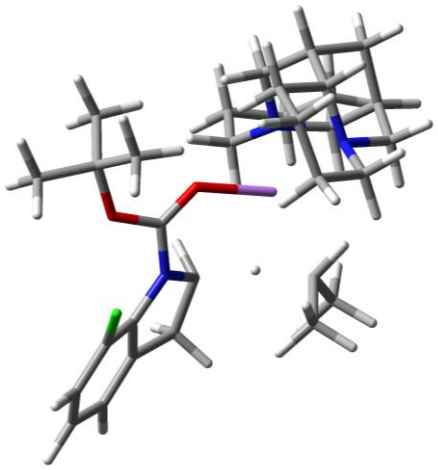

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0 1
 C                 -1.59328800    0.44623300   -0.58462100
 N                 -2.13911600   -0.70641400   -0.12625900
 C                 -1.27314300   -1.94837200   -0.20880000
 C                 -3.65788700   -2.43592900   -0.10646800
 C                 -2.29871900   -3.10088200   -0.15482600
 H                 -2.20219100   -3.78143600   -1.01350500
 H                 -2.18260600   -3.72947700    0.74069300
 O                 -0.36621300    0.67620700   -0.51099400
 C                  0.51747200   -1.95545700    2.04742100
 H                  1.41947100   -1.38137200    2.32349900
 C                 -0.54950100   -1.67962100    3.11402400
 H                 -0.72135600   -0.60246200    3.25244500
 H                 -0.30727300   -2.10092800    4.10540900
 H                 -1.51767800   -2.11049000    2.81860600
 C                  0.91125900   -3.43698500    2.02380900
 H                  1.18396500   -3.84099000    3.01402000
 H                  1.76353900   -3.62713200    1.35395200
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H	0.08188900	-4.05538900	1.65046900
Li	1.05006900	-0.30949200	0.48073900
H	1.24781700	2.50907200	-0.16881600
C	2.02379600	3.00794800	0.42094200
C	3.16146900	2.02300300	0.71241000
H	2.42208600	3.83054600	-0.18759700
C	1.41274800	3.54690000	1.72124800
N	2.68237500	0.89606100	1.55737400
H	3.93054700	2.58160100	1.28722700
C	3.88529300	1.50876000	-0.55450200
C	0.97325700	2.38056200	2.61336300
H	0.56717700	4.21017400	1.50438100
H	2.16071300	4.15290400	2.25304200
C	3.79270600	-0.03480500	1.86515100
C	2.12799200	1.40355300	2.83299700
C	3.05046200	0.64733000	-1.52490900
H	4.20080800	2.39853100	-1.11600400
C	5.11226000	0.70132700	-0.11755400
H	0.13043600	1.85392900	2.14797900
H	0.62416600	2.74246000	3.58808500
H	3.37555300	-0.88502700	2.41504800
H	4.51429800	0.46306400	2.54120300
C	4.57040300	-0.52423900	0.63179700
H	1.79312600	0.54062400	3.41774600
H	2.92737800	1.90375200	3.41406500
N	2.64591500	-0.66196800	-0.96392700
H	3.64696100	0.53047600	-2.44590800
H	2.13008000	1.16709000	-1.81209300
H	5.75246800	1.29838500	0.54450000
H	5.72446000	0.41624900	-0.98044300
C	3.75144200	-1.42801300	-0.31758700
H	5.40144500	-1.13308200	1.01167600
C	1.92400300	-1.49315800	-1.95754800
C	4.66958500	-2.16882900	-1.31964500
H	3.25327200	-2.19756400	0.28961600
H	1.16314000	-0.86019000	-2.42490200
C	2.81218600	-2.17486000	-3.00714800
H	1.38874000	-2.27060100	-1.39850800
H	5.37445200	-2.78861600	-0.75019800
H	5.27453400	-1.44990500	-1.88664500
C	3.87326900	-3.03093900	-2.30663300
H	2.18086400	-2.78881000	-3.66173500
H	3.29853100	-1.42835400	-3.64998800
H	3.37829500	-3.85014000	-1.76506700
H	4.54786300	-3.49729800	-3.03509700
C	-3.50342600	-1.03845000	0.00203100
C	-4.91157400	-3.02731100	-0.04726900
H	-5.00890300	-4.10552000	-0.14725500
C	-6.04027300	-2.23157400	0.17510900
C	-5.88808700	-0.86709300	0.40636400
H	-6.74431100	-0.24971000	0.65707900
C	-4.62283500	-0.27166300	0.35962600
H	-0.23982700	-1.85965100	0.85304100
H	-0.83442400	-1.90976300	-1.21555100
O	-2.47262800	1.23734000	-1.21618100
C	-2.14837600	2.55984400	-1.77405300
C	-1.06312900	2.43377700	-2.84959100

H	-1.35003000	1.67743800	-3.58833100
H	-0.10110500	2.15496900	-2.41922100
H	-0.95409000	3.39205200	-3.37006900
C	-1.75490800	3.52312400	-0.65230500
H	-2.56080700	3.60515200	0.08244200
H	-1.56584800	4.51857100	-1.07017000
H	-0.85104200	3.18419600	-0.14542200
C	-3.47440900	2.98310900	-2.41411400
H	-4.26888500	3.02655300	-1.66461300
H	-3.77111300	2.27054500	-3.19039800
H	-3.36727700	3.97188400	-2.87303600
H	-7.03016600	-2.67663100	0.21969500
Cl	-4.51665500	1.40017300	0.90748200

Structure: TS24

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*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
                14-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1982.4117213\MP2=-
1987.5047984\RMSD=4.304e-09\PG=C01 [X(C31H49Cl1Li1N3O2)]\\@
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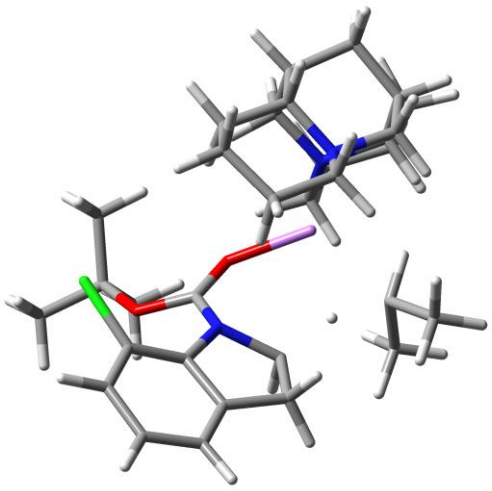

0 1

C	-1.43657900	0.87269300	-0.56732100
N	-2.08318400	-0.32620800	-0.68241100
C	-1.54754100	-1.23556000	-1.78288100
C	-3.83925800	-1.73259900	-1.18250500
C	-2.61501400	-2.33158500	-1.84749000
H	-2.79599000	-2.65177500	-2.88086500

H	-2.32976400	-3.23928400	-1.28889200
O	-0.19451000	0.95569800	-0.57898600
C	1.17771900	-2.02437400	-2.21668700
H	2.17129700	-1.81750800	-1.77459500
C	0.99182400	-3.54594700	-2.22756900
H	1.10571000	-3.99010700	-1.22804900
H	1.69396400	-4.07407400	-2.89569700
H	-0.02046500	-3.80486900	-2.57255800
C	1.19125600	-1.48394900	-3.65185200
H	1.91606400	-1.99242900	-4.31071900
H	1.41482700	-0.40791300	-3.69048200
H	0.20322300	-1.61192700	-4.11893000
Li	1.10487500	-0.53400000	-0.47166500
H	0.19464900	0.62941000	1.97552400
C	0.54139400	0.04689400	2.83657400
C	1.89710100	-0.59688200	2.51848900
H	0.67346100	0.74861100	3.67081000
C	-0.50531800	-1.01790000	3.19067600
N	1.76466200	-1.55573900	1.38784500
H	2.19834100	-1.16977900	3.42080600
C	3.03871200	0.41554500	2.27494600
C	-0.58436300	-2.06964700	2.07796100
H	-1.48526800	-0.55341300	3.34803900
H	-0.22369000	-1.50229100	4.13731900
C	3.06660800	-2.19230100	1.06770000
C	0.79930300	-2.62404900	1.74083200
C	2.89215000	1.33042100	1.04127600
H	3.06257900	1.07382600	3.15387900
C	4.35758200	-0.35814800	2.16258600
H	-1.02889300	-1.62626700	1.17984600
H	-1.23428500	-2.90155100	2.37644700
H	2.92847300	-2.79137500	0.16134900
H	3.34012300	-2.89264300	1.87947000
C	4.24388600	-1.21273700	0.89295800
H	0.73787600	-3.31102900	0.89089800
H	1.18937100	-3.20038900	2.60243400
N	2.97401700	0.60499500	-0.24607100
H	3.66686900	2.11196500	1.12268000
H	1.92583900	1.84476400	1.05466300
H	4.50530200	-0.99812300	3.04199600
H	5.21337500	0.32430400	2.11823100
C	4.14415800	-0.31022200	-0.35657300
H	5.14315300	-1.83086600	0.77027100
C	2.89474100	1.51906300	-1.40962000
C	5.47601400	0.41542000	-0.66308800
H	3.93249500	-0.95253200	-1.22306600
H	2.05004900	2.19298300	-1.24227400
C	4.18340700	2.29764200	-1.71269700
H	2.64423600	0.90547400	-2.28525800
H	6.25695000	-0.34037800	-0.81938600
H	5.79532400	1.02055500	0.19480600
C	5.35378800	1.32399500	-1.89418100
H	4.03093200	2.89990700	-2.61721000
H	4.40818600	3.00289000	-0.90078600
H	5.17816100	0.70882600	-2.78878100
H	6.29251900	1.86554300	-2.06357300
C	-3.44677300	-0.60471900	-0.42782100

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 C                  -5.14009700   -2.21148100   -1.13664400
 H                  -5.42346700   -3.07228200   -1.73724200
 C                  -6.07244800   -1.59908400   -0.29159500
 C                  -5.66652500   -0.56781600    0.55091800
 H                  -6.35782200   -0.13069100    1.26385800
 C                  -4.34959400   -0.09516000    0.51605800
 H                  -0.10471300   -1.58226100   -1.76180700
 H                  -1.64374300   -0.62231000   -2.69461800
 O                  -2.25853800    1.92569900   -0.52616200
 C                  -1.79721300    3.32402700   -0.43068800
 C                  -1.00673300    3.68486700   -1.69236000
 H                  -1.60853800    3.48824800   -2.58599100
 H                  -0.08280600    3.10887800   -1.76015900
 H                  -0.75795000    4.75204200   -1.67695100
 C                  -0.99162300    3.54593300    0.85183600
 H                  -1.55975400    3.20517800    1.72287000
 H                  -0.78940100    4.61627000    0.97269900
 H                  -0.03921100    3.01499800    0.82032200
 C                  -3.11490300    4.10276700   -0.38239100
 H                  -3.69672100    3.82554600    0.50085700
 H                  -3.71696100    3.89166900   -1.27161700
 H                  -2.91112100    5.17836900   -0.34787400
 H                  -7.09873600   -1.95286500   -0.25138900
 Cl                 -3.88568900    1.04173700    1.78566100
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Structure: TS25

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               14-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1982.4241452\MP2= -
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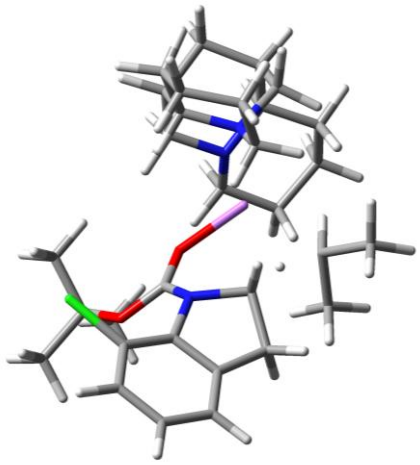

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C	-1.51287300	-0.63108800	-0.43939700
N	-2.10537800	0.02966400	0.59175200
C	-1.48999300	0.00658600	1.97026700
C	-3.88546600	-0.26219900	2.03919400
C	-2.62191800	-0.66749400	2.77952200
H	-2.53016200	-1.76476600	2.78709200
H	-2.62762600	-0.34019600	3.82530200
O	-0.28049300	-0.74799500	-0.56578400
C	1.01757200	-1.24214000	2.66436400
C	0.53967600	-2.69087700	2.82683000
H	1.18221600	-3.30419200	3.48327900
H	0.46357600	-3.21673400	1.86346100
H	-0.46496200	-2.71461000	3.27142100
C	1.12441600	-0.55313100	4.02852900
H	1.65452100	-1.14949100	4.79163500
H	0.12302400	-0.34459100	4.43792600
H	1.64314800	0.41469800	3.96397700
Li	1.22978800	-0.37075200	0.58508600
H	4.04923000	-1.00428900	1.84025500
C	4.73937800	-1.25196400	1.02574500
C	4.34783800	-0.49298500	-0.24844300
H	5.73797500	-0.91780000	1.33642600
C	4.73272300	-2.76807100	0.78894600
N	3.00959500	-0.91916500	-0.73692800
H	5.09664200	-0.76977700	-1.02131300
C	4.43781700	1.04406000	-0.12060900
C	3.38342000	-3.20943100	0.20901600
H	4.94417800	-3.30298800	1.72229100
H	5.53722500	-3.02747300	0.08502300
C	2.65250500	-0.20837400	-1.98852800
C	3.00912900	-2.37306000	-1.01478500
C	3.44861800	1.71067700	0.85723400
H	5.44664100	1.26762800	0.25172700
C	4.24539400	1.65486000	-1.51337400
H	2.60331300	-3.11521400	0.97142200
H	3.41565400	-4.26606400	-0.08490200
H	1.62112900	-0.47897000	-2.23156800

H	3.29307400	-0.57370900	-2.81447300
C	2.80565800	1.32335500	-1.92904800
H	2.00921700	-2.64352800	-1.37068100
H	3.71707700	-2.59104300	-1.83890600
N	2.03428400	1.63974200	0.42464600
H	3.78135700	2.75398300	0.99085800
H	3.50454300	1.23927200	1.84496100
H	4.95861100	1.22050500	-2.22565900
H	4.42706900	2.73489700	-1.49997300
C	1.79737400	2.03019700	-0.99532200
H	2.61078200	1.69138500	-2.94523700
C	1.13762600	2.38548700	1.34192400
C	1.77475400	3.55973600	-1.23210000
H	0.79188600	1.65457600	-1.23353900
H	1.39007800	2.09248800	2.36580100
C	1.15570600	3.91129500	1.17427000
H	0.11828500	2.03034700	1.15522000
H	1.48784300	3.74465100	-2.27572400
H	2.77879500	3.98387600	-1.10483800
C	0.81329300	4.27571100	-0.27470800
H	0.43150100	4.35137700	1.87106900
H	2.13868600	4.32278900	1.44208600
H	-0.22025600	3.96923700	-0.49099200
H	0.85976600	5.36059600	-0.43003000
C	-3.52095600	0.14799200	0.74440500
C	-5.20829000	-0.20157400	2.45484000
H	-5.48699700	-0.53067900	3.45260300
C	-6.17684700	0.31291500	1.58245500
C	-5.81390900	0.78041100	0.32148600
H	-6.55156500	1.22275900	-0.33987500
C	-4.47874500	0.71352000	-0.09525900
H	-0.15482200	-0.58442200	2.11589200
O	-2.40340000	-1.14220700	-1.30350300
C	-2.04334600	-1.78454800	-2.57666900
C	-1.19967900	-3.03702100	-2.31892200
H	-1.71201100	-3.69969800	-1.61321400
H	-0.22251500	-2.78098400	-1.90866000
H	-1.05868600	-3.58373600	-3.25830400
C	-1.34556100	-0.77802400	-3.49545800
H	-1.97365800	0.10732300	-3.63303100
H	-1.17244100	-1.23375100	-4.47691900
H	-0.38387600	-0.46587500	-3.08520800
C	-3.41145600	-2.17271700	-3.14625700
H	-4.03591700	-1.28597000	-3.28699800
H	-3.93029100	-2.85571400	-2.46629000
H	-3.28574700	-2.67274000	-4.11252700
H	-7.21499800	0.38005100	1.89616800
Cl	-4.05229800	1.45206900	-1.63703500
H	-1.45520300	1.05936900	2.28924800
H	2.04287900	-1.27839600	2.24518100

Structure: TS26

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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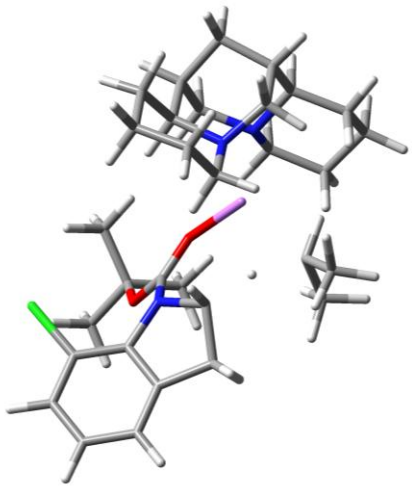

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0 1
 C                  1.54788100    0.74289500   -0.16425100
 N                  2.09835800   -0.35607800    0.42120800
 C                  1.46789100   -0.95557400    1.65458700
 C                  3.87439900   -0.88791200    1.80392800
 C                  2.62738700   -0.82131200    2.66936200
 H                  2.59862200    0.13800400    3.20866500
 H                  2.60022400   -1.61371900    3.42574400
 O                  0.32268100    0.95115300   -0.21880600
 C                 -0.91129700    0.13916400    2.89367800
 C                 -0.31472100    1.41415100    3.50463200
 H                 -0.89943000    1.82384700    4.34739500
 H                 -0.20270700    2.21954900    2.76389200
 H                  0.69233900    1.21623200    3.89787800
 C                 -1.04616000   -0.95475600    3.95743000
 H                 -1.51050600   -0.61070300    4.89828100
 H                 -0.05722300   -1.35779400    4.22864900
 H                 -1.64334200   -1.80700100    3.60187800
 Li                -1.19461300    0.10685100    0.65061600
 H                 -3.96694500    0.57706000    2.05160500
 C                 -4.60330100    1.14549500    1.36350100
 C                 -4.26369200    0.78697500   -0.08858900
```

H	-5.64076000	0.84597200	1.56136400
C	-4.42040500	2.64681900	1.61843500
N	-2.87460400	1.19121400	-0.43109600
H	-4.95862300	1.37286500	-0.72750800
C	-4.52089600	-0.69309200	-0.44605400
C	-3.01281300	3.08469200	1.19969700
H	-4.59902400	2.88141400	2.67439700
H	-5.16748400	3.20740100	1.03751200
C	-2.55816000	0.86982100	-1.84395000
C	-2.70385200	2.64830600	-0.23328300
C	-3.63232700	-1.73207000	0.26820700
H	-5.55704000	-0.91056200	-0.15417700
C	-4.35642700	-0.85828200	-1.96160600
H	-2.27287300	2.65325800	1.88246600
H	-2.91010700	4.17512100	1.26564200
H	-1.49508700	1.07887600	-1.99457300
H	-3.12679200	1.54541700	-2.51152600
C	-2.87898900	-0.57604000	-2.26454400
H	-1.67167600	2.89827500	-0.49619900
H	-3.36329900	3.19709900	-0.93478600
N	-2.20722000	-1.68691700	-0.13274300
H	-4.07689200	-2.72319300	0.07552600
H	-3.66165400	-1.58439400	1.35379100
H	-4.99789900	-0.14728900	-2.49802700
H	-4.65461000	-1.86132000	-2.28537700
C	-1.97754000	-1.64389500	-1.60599000
H	-2.69760400	-0.62933200	-3.34630600
C	-1.42648700	-2.77735200	0.50002700
C	-2.11218400	-3.01714800	-2.30768800
H	-0.93039800	-1.32790300	-1.72778500
H	-1.67541300	-2.78964500	1.56538700
C	-1.60834400	-4.16336300	-0.13340100
H	-0.36974400	-2.50044500	0.42899600
H	-1.81390900	-2.89903300	-3.35785900
H	-3.15954100	-3.34434700	-2.31686200
C	-1.26446000	-4.09857600	-1.62573500
H	-0.95899000	-4.87761800	0.38804800
H	-2.63838400	-4.52211300	-0.00130800
H	-0.19737800	-3.85894600	-1.74166200
H	-1.42422900	-5.06921500	-2.11106800
C	3.50295100	-0.60218500	0.47807500
C	5.18759400	-1.21037800	2.11683900
H	5.47280400	-1.42011300	3.14457000
C	6.13707900	-1.28693900	1.08900700
C	5.76427700	-1.06456000	-0.23471300
H	6.48535600	-1.16710600	-1.03893100
C	4.43916800	-0.73642100	-0.54581200
H	0.19300000	-0.38400100	2.09097200
O	2.47253900	1.57085900	-0.67267800
C	2.16509300	2.80305300	-1.41385300
C	1.46371900	3.80014100	-0.48616900
H	2.07802900	3.99045900	0.40033700
H	0.49273300	3.42408600	-0.16119400
H	1.31712300	4.75166000	-1.00986400
C	1.35146900	2.48824200	-2.67170600
H	1.85058300	1.71069700	-3.25861300
H	1.27331800	3.38876800	-3.29136600

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 H                     0.34467500    2.15133400   -2.42266300
 C                     3.55871200    3.31435700   -1.79252600
 H                     4.07328700    2.59381200   -2.43472300
 H                     4.16578900    3.47156800   -0.89560000
 H                     3.47477500    4.26631500   -2.32756200
 H                     7.16676900   -1.55063800    1.31457200
 Cl                    3.99107400   -0.60813200   -2.24491600
 H                     1.36508700   -2.02909600    1.43664200
 H                    -1.94026800    0.38495000    2.55813400
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Structure: TS27

```
 ****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
                14-Feb-2011
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
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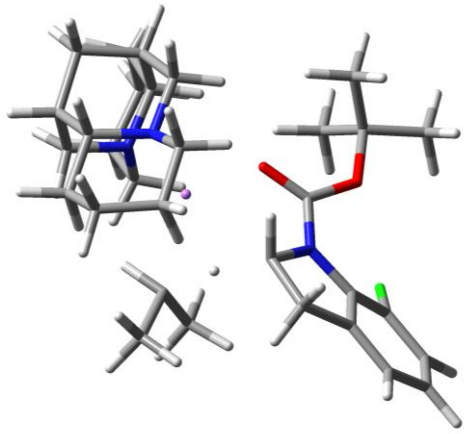

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 N                    -2.12291900   -0.53399000   -0.33402900
 C                    -1.32331500   -1.80258200   -0.48621800
 C                    -3.71355700   -2.18874700   -0.35652400
 C                    -2.41035300   -2.88486800   -0.68214500
 H                    -2.42944900   -3.29150300   -1.70657400
 H                    -2.27030700   -3.74739300   -0.01679000
 O                    -0.27230000    0.73604800   -0.67036200
 C                     0.22717500   -1.88935200    1.96576000
 H                     1.23604200   -1.49994200    2.21115200
 C                    -0.78754100   -1.20307500    2.88948100
 H                    -0.74189500   -0.10722500    2.82310600
 H                    -0.66969900   -1.46851100    3.95542800
 H                    -1.81359700   -1.48873500    2.61189400
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C	0.24325100	-3.39912800	2.23697600
H	0.40882500	-3.65601500	3.29794800
H	1.01567800	-3.92352500	1.65703700
H	-0.71961800	-3.85214600	1.95705200
Li	0.98896000	-0.55319300	0.20729600
H	2.86914900	-2.71690900	0.97346500
C	3.56469200	-2.91661000	0.15098800
C	3.82025500	-1.62963800	-0.64222100
H	4.51120300	-3.24663100	0.59898400
C	2.98853500	-4.01338900	-0.75395900
N	2.55753200	-1.14148600	-1.26086300
H	4.52172800	-1.89313200	-1.46220300
C	4.53372600	-0.52291000	0.16526200
C	1.74212100	-3.49543300	-1.48118400
H	2.74739800	-4.90745500	-0.16705900
H	3.74875600	-4.31198800	-1.49073100
C	2.77316700	0.11132800	-2.02547900
C	2.02854600	-2.16915700	-2.18645800
C	3.76298400	0.04706700	1.37267400
H	5.45340700	-0.97338700	0.56230400
C	4.88183600	0.62353200	-0.79098100
H	0.92536300	-3.35582000	-0.76464100
H	1.39669000	-4.22337900	-2.22613700
H	1.78861000	0.48007000	-2.33290400
H	3.34327800	-0.11339100	-2.94716800
C	3.54355400	1.20655900	-1.26368700
H	1.11469300	-1.77126700	-2.64114800
H	2.75377200	-2.33312100	-3.00758900
N	2.54812300	0.80001500	0.99035400
H	4.46957400	0.67052000	1.94676100
H	3.44383400	-0.75795800	2.04396100
H	5.45876400	0.24880000	-1.64637500
H	5.50238400	1.37793600	-0.29508200
C	2.77107400	1.82042100	-0.07419600
H	3.71700800	2.01741800	-1.98394600
C	1.86751000	1.39370200	2.16588800
C	3.43892700	3.11985400	0.43685600
H	1.76753800	2.08948200	-0.42640000
H	1.77815300	0.61435800	2.92900000
C	2.53698400	2.65289000	2.73559800
H	0.84720200	1.64946600	1.85119200
H	3.47259800	3.84239300	-0.38941300
H	4.48019700	2.93226400	0.72765300
C	2.68808500	3.71146600	1.63739900
H	1.92947100	3.03308300	3.56636100
H	3.52210500	2.40753100	3.15534300
H	1.69068300	4.04684200	1.31814700
H	3.21145400	4.59813900	2.01591600
C	-3.48214200	-0.82101900	-0.10236800
C	-4.98014300	-2.73939200	-0.22944700
H	-5.13876900	-3.79349500	-0.44250400
C	-6.04035200	-1.93503300	0.20136300
C	-5.80186300	-0.61252100	0.56386800
H	-6.59806100	0.00051000	0.97279900
C	-4.52099100	-0.05914700	0.45268600
H	-0.43053100	-1.85044100	0.66604400
H	-0.75685800	-1.67435400	-1.41828400

O	-2.36418100	1.58510400	-1.07587500
C	-1.93585900	2.94994500	-1.42230900
C	-0.99843500	2.91416100	-2.63491900
H	-1.46900200	2.36928900	-3.46056800
H	-0.05116700	2.43165000	-2.39190100
H	-0.79936200	3.93754300	-2.97323300
C	-1.29887100	3.63342500	-0.20944100
H	-1.98626200	3.62004800	0.64161200
H	-1.07369400	4.67809800	-0.45288200
H	-0.37130600	3.13669000	0.07982800
C	-3.25719500	3.62894800	-1.79550300
H	-3.94723300	3.62459000	-0.94771500
H	-3.73448600	3.10596300	-2.63038800
H	-3.07176800	4.66581800	-2.09570100
H	-7.04009400	-2.34737900	0.30267300
Cl	-4.28364900	1.52841600	1.17539500

Structure: TS28

```
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 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               14-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
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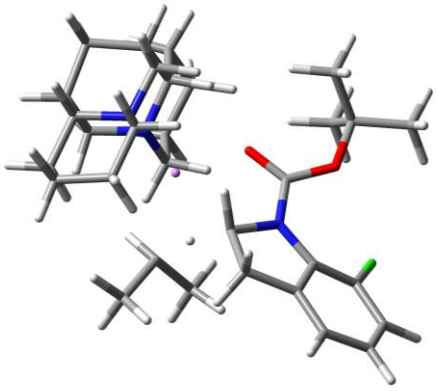

0 1

C	-1.51922500	0.62907800	-0.66276200
N	-2.12291500	-0.53397900	-0.33402000
C	-1.32329300	-1.80255900	-0.48620100
C	-3.71353100	-2.18875800	-0.35652900
C	-2.41031000	-2.88486400	-0.68211300
H	-2.42938400	-3.29152600	-1.70653100
H	-2.27025800	-3.74736900	-0.01673000
O	-0.27230100	0.73608400	-0.67029500

C	0.22718500	-1.88931700	1.96579900
H	1.23604800	-1.49988400	2.21117300
C	-0.78753300	-1.20300600	2.88949300
H	-0.74191000	-0.10715900	2.82304900
H	-0.66966800	-1.46837200	3.95545600
H	-1.81358700	-1.48870500	2.61194200
C	0.24327600	-3.39907800	2.23709200
H	0.40893600	-3.65591300	3.29806300
H	1.01564900	-3.92351100	1.65711400
H	-0.71962100	-3.85210200	1.95727100
Li	0.98895600	-0.55319100	0.20731500
H	2.86912600	-2.71691500	0.97347200
C	3.56466300	-2.91662800	0.15099300
C	3.82022600	-1.62966800	-0.64223500
H	4.51117600	-3.24664900	0.59898500
C	2.98849400	-4.01341400	-0.75393800
N	2.55749700	-1.14151400	-1.26086600
H	4.52168400	-1.89317800	-1.46222400
C	4.53372100	-0.52293700	0.16522300
C	1.74207500	-3.49546100	-1.48115700
H	2.74735900	-4.90747400	-0.16702700
H	3.74870800	-4.31202300	-1.49071400
C	2.77312900	0.11129100	-2.02549700
C	2.02849800	-2.16919200	-2.18644500
C	3.76300500	0.04706200	1.37264200
H	5.45340500	-0.97341800	0.56225400
C	4.88182500	0.62348900	-0.79104100
H	0.92532300	-3.35584100	-0.76461000
H	1.39663800	-4.22341200	-2.22610300
H	1.78856900	0.48004000	-2.33290900
H	3.34322100	-0.11344100	-2.94719400
C	3.54353900	1.20652400	-1.26373000
H	1.11464200	-1.77130300	-2.64113000
H	2.75371500	-2.33316500	-3.00758200
N	2.54814500	0.80001700	0.99033400
H	4.46961200	0.67051300	1.94671000
H	3.44385800	-0.75795300	2.04394300
H	5.45873300	0.24874000	-1.64644100
H	5.50238900	1.37789400	-0.29516300
C	2.77108700	1.82040800	-0.07423300
H	3.71698900	2.01737200	-1.98400200
C	1.86756000	1.39372900	2.16587200
C	3.43896300	3.11984100	0.43678900
H	1.76754800	2.08947500	-0.42642200
H	1.77820600	0.61439500	2.92899600
C	2.53705800	2.65291500	2.73555300
H	0.84724900	1.64950000	1.85119000
H	3.47262600	3.84236900	-0.38949000
H	4.48023800	2.93224500	0.72756900
C	2.68815000	3.71147600	1.63733900
H	1.92956600	3.03312600	3.56632400
H	3.52218500	2.40755000	3.15528300
H	1.69074500	4.04685800	1.31810100
H	3.21153500	4.59814800	2.01583500
C	-3.48213900	-0.82102300	-0.10238000
C	-4.98011100	-2.73941900	-0.22947500
H	-5.13871600	-3.79352700	-0.44252700

C	-6.04034200	-1.93507300	0.20130400
C	-5.80187800	-0.61255500	0.56380400
H	-6.59809300	0.00046700	0.97271400
C	-4.52101100	-0.05916300	0.45264800
H	-0.43053300	-1.85043000	0.66607500
H	-0.75683700	-1.67433100	-1.41826800
O	-2.36418100	1.58512500	-1.07583600
C	-1.93586000	2.94997100	-1.42225300
C	-0.99842300	2.91419800	-2.63485400
H	-1.46897700	2.36932400	-3.46050900
H	-0.05115400	2.43169500	-2.39182800
H	-0.79935600	3.93758300	-2.97316400
C	-1.29888500	3.63344500	-0.20937400
H	-1.07370100	4.67811700	-0.45280900
H	-0.37132600	3.13670500	0.07990400
H	-1.98628800	3.62006900	0.64166900
C	-3.25719300	3.62897400	-1.79545700
H	-3.94724700	3.62459100	-0.94768200
H	-3.73446500	3.10600700	-2.63036300
H	-3.07176700	4.66585300	-2.09562600
H	-7.04008100	-2.34743100	0.30259300
Cl	-4.28371300	1.52840600	1.17535700

Structure: TS29

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 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               14-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1982.4266484\MP2=-
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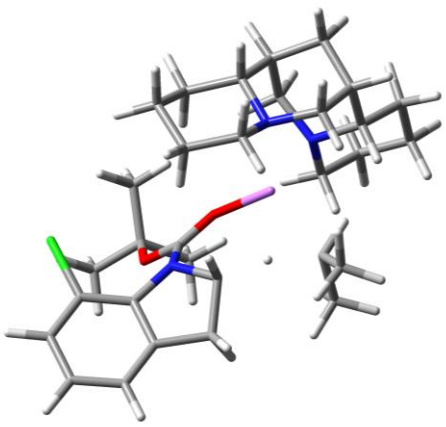

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C	1.50295100	0.71741400	0.24294900
N	2.14404600	-0.48140400	0.32741000
C	1.53598600	-1.61662800	1.11434100
C	3.91435600	-1.43312700	1.47033300
C	2.63551600	-1.85554200	2.17476100
H	2.48447600	-1.23968300	3.07492000
H	2.66567700	-2.90022700	2.50382000
O	0.26500400	0.83108600	0.21676400
C	-1.02541500	-1.58011700	2.43897300
C	-0.67073200	-0.81399300	3.71956700
H	-1.32127200	-1.05444800	4.57922600
H	-0.71302600	0.27584600	3.57640100
H	0.35618400	-1.04468900	4.03707200
C	-1.02539500	-3.09104200	2.69197600
H	0.00146900	-3.45898000	2.84614000
H	-1.43055600	-3.65383000	1.83736300
H	-1.60244600	-3.39877800	3.58147200
Li	-1.13070600	-0.48693200	0.43761400
H	-0.50341400	0.44774100	-2.26440000
C	-0.98130000	-0.19018400	-3.01689500
C	-2.27637900	-0.78560600	-2.45101800
H	-1.23312600	0.44542100	-3.87609100
C	-0.01491900	-1.30563700	-3.43365500
N	-1.98918600	-1.62745700	-1.25741900
H	-2.69385300	-1.44439500	-3.24169300
C	-3.37993500	0.25451800	-2.16311000
C	0.23743100	-2.23791900	-2.24470900
H	0.93055300	-0.88386100	-3.79408100
H	-0.45203300	-1.87124000	-4.26970900
C	-3.23450200	-2.21800900	-0.70327200
C	-1.07263000	-2.73350200	-1.62815100
C	-3.07805800	1.28035900	-1.05062000
H	-3.51716200	0.82681300	-3.09039500
C	-4.66914300	-0.49895000	-1.81596800
H	0.82321800	-1.70584800	-1.48928600
H	0.82974200	-3.10934900	-2.55028900
H	-2.97645300	-2.70848000	0.24213000
H	-3.60018600	-3.00720300	-1.38706400
C	-4.39446100	-1.22271600	-0.49158700
H	-0.86893500	-3.31574400	-0.72292500
H	-1.58416300	-3.40734000	-2.34286700
N	-3.00272000	0.68280700	0.30153700
H	-3.85375700	2.06275200	-1.11015300
H	-2.11863700	1.77636800	-1.23398400
H	-4.91403700	-1.22213500	-2.60447200
H	-5.52115400	0.18490900	-1.73616000
C	-4.15551300	-0.19884200	0.63807100
H	-5.26525100	-1.82481500	-0.19971400
C	-2.78294700	1.70334400	1.35255700
C	-5.43971300	0.57487600	1.01906300
H	-3.85018900	-0.75250300	1.53688300
H	-1.96595100	2.35009100	1.01845100
C	-4.02387600	2.52622200	1.73125300
H	-2.42706200	1.17479200	2.24643900
H	-6.20316700	-0.14886100	1.33366500

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 H                 -5.85059800    1.10265100    0.14930500
 C                 -5.17060300    1.59215700    2.13634000
 H                 -3.76254300    3.20462500    2.55317900
 H                 -4.33786800    3.16000700    0.89040300
 H                 -4.89572000    1.05984500    3.05864000
 H                 -6.08013300    2.16266600    2.36099900
 C                  3.56428900   -0.62096200    0.37698400
 C                  5.24171700   -1.75824900    1.71256600
 H                  5.51021200   -2.37722800    2.56477900
 C                  6.23011800   -1.30154600    0.83015300
 C                  5.88422200   -0.55030600   -0.29083300
 H                  6.64008100   -0.23477300   -1.00241000
 C                  4.54434200   -0.22120800   -0.52970900
 H                  0.18080600   -1.45147100    1.63408300
 O                  2.34935100    1.75530700    0.18394900
 C                  1.91844700    3.15275300    0.01838400
 C                  1.12859500    3.59432200    1.25424900
 H                  1.72597500    3.44406500    2.15982000
 H                  0.20014000    3.03006000    1.35141700
 H                  0.88800500    4.66078800    1.17745500
 C                  1.12693600    3.32718800   -1.28115800
 H                  1.69573000    2.93004300   -2.12805600
 H                  0.95018800    4.39412600   -1.45883100
 H                  0.16336700    2.81784500   -1.23313300
 C                  3.25287100    3.90048100   -0.06110100
 H                  3.83371600    3.56468100   -0.92484400
 H                  3.84526000    3.72294800    0.84187000
 H                  3.07334100    4.97697700   -0.15362800
 H                  7.27267000   -1.55809100    0.99729500
 Cl                 4.14481100    0.59966200   -2.03666400
 H                  1.54921100   -2.48346800    0.43584100
 H                 -2.06036000   -1.29814000    2.16478000
```

Structure: TS30

```
 ****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1982.4266469\MP2=-
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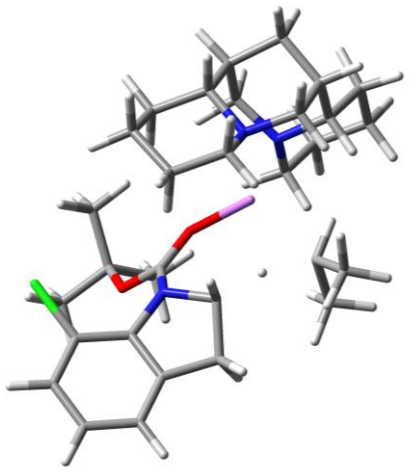

0 1

C	1.50290600	0.71729500	0.24351300
N	2.14396900	-0.48158800	0.32728500
C	1.53590300	-1.61724700	1.11357800
C	3.91430700	-1.43401200	1.46956600
C	2.63549400	-1.85686900	2.17377900
H	2.48450400	-1.24163100	3.07437100
H	2.66567000	-2.90178300	2.50211000
O	0.26496400	0.83100400	0.21740700
C	-1.02562700	-1.58172800	2.43809400
C	-0.67095700	-0.81678100	3.71938700
H	-1.32137500	-1.05815300	4.57888300
H	-0.71344500	0.27319500	3.57726500
H	0.35602400	-1.04760800	4.03657300
C	-1.02560000	-3.09287600	2.68977200
H	0.00124200	-3.46091500	2.84383100
H	-1.43056300	-3.65493500	1.83458700
H	-1.60282000	-3.40141000	3.57888300
Li	-1.13062800	-0.48722500	0.43748200
H	-0.50308300	0.44955700	-2.26370400
C	-0.98083400	-0.18777400	-3.01678700
C	-2.27598200	-0.78368800	-2.45158500
H	-1.23255200	0.44851200	-3.87551000
C	-0.01436900	-1.30288100	-3.43430700
N	-1.98894800	-1.62649200	-1.25862200
H	-2.69331900	-1.44185500	-3.24285000
C	-3.37962900	0.25616200	-2.16301700
C	0.23781800	-2.23611800	-2.24608000
H	0.93114700	-0.88080900	-3.79427300
H	-0.45137100	-1.86781500	-4.27087100
C	-3.23433200	-2.21753500	-0.70516200
C	-1.07233700	-2.73222500	-1.63015400
C	-3.07799600	1.28111600	-1.04964600
H	-3.51673100	0.82919300	-3.08986500
C	-4.66885800	-0.49765700	-1.81669500
H	0.82346600	-1.70464200	-1.49012900
H	0.83021300	-3.10728000	-2.55226200

H	-2.97643500	-2.70880300	0.23986700
H	-3.59990100	-3.00614900	-1.38968800
C	-4.39434800	-1.22244900	-0.49283700
H	-0.86879400	-3.31526100	-0.72540600
H	-1.58376300	-3.40544000	-2.34553400
N	-3.00277600	0.68247800	0.30203300
H	-3.85376700	2.06347800	-1.10864100
H	-2.11860200	1.77737600	-1.23247700
H	-4.91355000	-1.22025200	-2.60580000
H	-5.52093400	0.18607900	-1.73651500
C	-4.15560400	-0.19947500	0.63767600
H	-5.26515300	-1.82481600	-0.20155700
C	-2.78319300	1.70215900	1.35392500
C	-5.43987800	0.57392200	1.01903900
H	-3.85043600	-0.75385500	1.53609800
H	-1.96615900	2.34920200	1.02047600
C	-4.02419600	2.52470200	1.73312700
H	-2.42742600	1.17287900	2.24742300
H	-6.20339500	-0.15007300	1.33289100
H	-5.85058500	1.10240000	0.14962500
C	-5.17100500	1.59028700	2.13719800
H	-3.76299900	3.20237500	2.55569800
H	-4.33802600	3.15924400	0.89278700
H	-4.89630900	1.05721700	3.05911800
H	-6.08058200	2.16060900	2.36214400
C	3.56420500	-0.62121000	0.37670700
C	5.24168200	-1.75925600	1.71156900
H	5.51021500	-2.37873000	2.56341100
C	6.23004800	-1.30203300	0.82938600
C	5.88410700	-0.55015600	-0.29116100
H	6.63993900	-0.23421200	-1.00258400
C	4.54421800	-0.22092900	-0.52979800
H	0.18076800	-1.45235800	1.63344400
O	2.34932400	1.75520100	0.18509300
C	1.91841700	3.15275200	0.02036700
C	1.12867900	3.59358100	1.25656900
H	1.72623100	3.44301000	2.16197500
H	0.20035300	3.02907900	1.35360800
H	0.88785800	4.66003400	1.18032200
C	1.12678100	3.32796800	-1.27899600
H	1.69541200	2.93116700	-2.12616500
H	0.95019800	4.39502700	-1.45610400
H	0.16313200	2.81876300	-1.23112400
C	3.25284200	3.90050800	-0.05880900
H	3.83357100	3.56525500	-0.92284300
H	3.84534200	3.72238400	0.84397100
H	3.07332100	4.97706800	-0.15062000
H	7.27260800	-1.55866200	0.99634500
Cl	4.14460900	0.60079300	-2.03626700
H	1.54898300	-2.48368300	0.43456200
H	-2.06058000	-1.29950800	2.16416000

Structure: TS31

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               23-Aug-2010
```

```
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1580.7366985\MP2=-
1584.8437671\RMSD=8.623e-09\PG=C01 [X(C26H48Li1N3S1)]\\@
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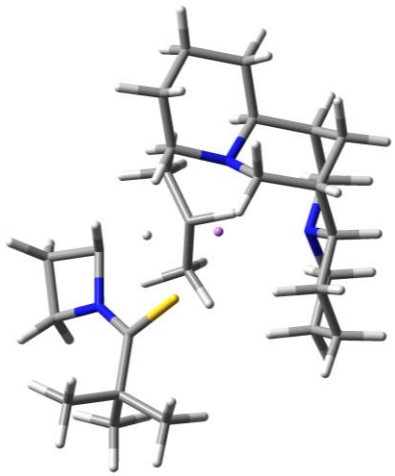

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0 1
 H                 -4.86885200   -2.34304300   -0.07303400
 C                 -4.00372500   -2.14358400    0.56556900
 N                 -2.98910800   -1.26497400   -0.07630000
 C                 -2.93513100   -3.25612900    0.64821500
 C                 -1.90545600   -2.20594300    0.16260600
 H                 -1.34547700   -2.42885400   -0.75178300
 H                 -0.98605600   -1.67273700    1.07909500
 H                 -4.34432000   -1.75449100    1.52858000
 H                 -2.77271300   -3.66967000    1.64748300
 H                 -3.13043200   -4.08276800   -0.04544900
 C                 -2.98013300   -0.08458200   -0.66752900
 S                 -1.47502300    0.46105800   -1.33073000
 C                 -4.29567700    0.70430800   -0.87262300
 C                 -5.09247100    0.02843900   -2.01671300
 H                 -6.02395600    0.57686600   -2.20446700
 H                 -5.35715900   -1.00753400   -1.77998300
 H                 -4.50640500    0.02407500   -2.94172000
 C                 -5.15499400    0.75435100    0.41390400
 H                 -5.98655600    1.45335900    0.26616400
 H                 -4.56812300    1.10972500    1.26859300
 H                 -5.59426800   -0.20983500    0.67769800
 C                 -4.01398300    2.16325400   -1.28542900
 H                 -4.96857300    2.68172000   -1.43777400
 H                 -3.43477800    2.21756400   -2.20890400
 H                 -3.45372700    2.69568400   -0.51023200
 C                 -0.20227000   -1.29143200    2.28474200
 H                  0.62351900   -0.56346400    2.38153100
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C	-1.33232200	-0.82197400	3.20661100
H	-1.62670300	0.21658500	2.99910900
H	-1.08372600	-0.88209300	4.28115200
H	-2.23419300	-1.43738200	3.06551700
C	0.33799600	-2.65766400	2.71735700
H	1.23056000	-2.95022100	2.14520300
H	-0.40916600	-3.44722100	2.54813100
H	0.61029000	-2.71013900	3.78641900
H	0.28489500	2.44907700	-1.27698700
C	0.96522800	3.16830900	-0.81079400
C	2.13609500	2.44289100	-0.13758600
H	1.36970300	3.80233800	-1.61085000
C	0.17802400	4.01500200	0.19736100
N	1.67736200	1.60498600	1.00597900
H	2.80499700	3.23044500	0.27016000
C	3.01101500	1.61898200	-1.11143800
C	-0.24981800	3.14886500	1.38759200
H	-0.69728500	4.46332300	-0.28688700
H	0.80597600	4.84470000	0.55500800
C	2.84063800	0.97669700	1.67834600
C	0.95505400	2.43377300	1.99875700
C	2.34919700	0.38527000	-1.76237500
H	3.28778000	2.29533200	-1.93123000
C	4.26699500	1.16257300	-0.36079900
H	-0.98627600	2.40788800	1.05251800
H	-0.72924100	3.75875900	2.16364000
H	2.45929200	0.31410200	2.46307800
H	3.43832700	1.75972700	2.18309900
C	3.78272800	0.20476900	0.73644300
H	0.63940700	1.77517700	2.81579400
H	1.64718200	3.18227100	2.43205200
N	2.03378100	-0.70116300	-0.80311000
H	3.03021500	0.03785000	-2.55768700
H	1.40935000	0.65975900	-2.25357900
H	4.78520300	2.02165500	0.08424400
H	4.97891900	0.67847300	-1.03831400
C	3.15490700	-1.06176600	0.11195800
H	4.62983500	-0.12831500	1.35086700
C	1.48584100	-1.90145600	-1.48204900
C	4.22808700	-1.96996200	-0.53688400
H	2.69369900	-1.64706700	0.92086600
H	0.70109100	-1.56416100	-2.16591500
C	2.52528700	-2.77743600	-2.19467500
H	0.99417800	-2.50836400	-0.71049400
H	4.94458900	-2.26779700	0.24003000
H	4.79983800	-1.41349400	-1.29023500
C	3.61060800	-3.20698300	-1.20149000
H	2.01827400	-3.65044300	-2.62463100
H	2.97949400	-2.23444500	-3.03488100
H	3.16219400	-3.85336800	-0.43263700
H	4.38834500	-3.80062300	-1.69757800
Li	0.32221600	-0.08307900	0.35015100

Structure: TS32

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
```

```
                23-Aug-2010
 ******************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
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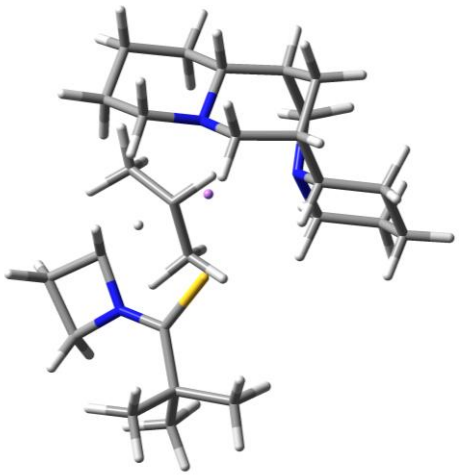

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 H                -5.11133700   -1.65737900   -0.28555700
 C                -4.22303200   -1.66936300    0.35228300
 N                -3.10291900   -0.84996200   -0.18312200
 C                -3.31525300   -2.91490000    0.24928400
 C                -2.15443200   -1.95345500   -0.10938900
 H                -1.64286700   -2.11716300   -1.06518300
 H                -1.17512700   -1.70218600    0.85710500
 H                -4.50172100   -1.38206500    1.36945900
 H                -3.20313200   -3.48444000    1.17592300
 H                -3.62518200   -3.60016800   -0.54841900
 C                -2.93790200    0.39224500   -0.59892400
 S                -1.37911400    0.82302600   -1.21543800
 C                -4.13297900    1.37405100   -0.64369400
 C                -5.02975400    0.99181600   -1.84782900
 H                -5.87873500    1.68282000   -1.92122500
 H                -5.43234300   -0.02269100   -1.75779300
 H                -4.46184200    1.04818900   -2.78239600
 C                -4.96057300    1.34545900    0.66422700
 H                -5.68070400    2.17187400    0.65450200
 H                -4.31784500    1.47212400    1.54280800
 H                -5.53526100    0.42558000    0.79004000
 C                -3.65459500    2.82607900   -0.84614000
 H                -4.52881800    3.48725300   -0.88909600
```

H	-3.08497800	2.93910400	-1.77035700
H	-3.01546400	3.15349400	-0.01999200
C	-0.35773100	-1.50853800	2.10778400
H	0.62661200	-1.00924200	2.21048600
C	-1.36402700	-0.74791800	2.97876200
H	-1.42760000	0.31512600	2.71097600
H	-1.14565700	-0.80104100	4.06047900
H	-2.37536800	-1.16446200	2.85112700
C	-0.19620300	-2.94632100	2.61225900
H	0.58943100	-3.49460900	2.07528300
H	-1.12580300	-3.51718200	2.47184900
H	0.04637400	-3.01104800	3.68806800
H	2.34926800	-2.28070900	1.19921600
C	3.03035200	-2.55241300	0.38457500
C	3.19297100	-1.37097700	-0.57923500
H	4.00589100	-2.76995400	0.83886800
C	2.48949600	-3.78874600	-0.34450400
N	1.89681400	-1.04167800	-1.23155000
H	3.90016100	-1.69937600	-1.37006700
C	3.84204800	-0.12276300	0.06044000
C	1.19366500	-3.43592100	-1.08348000
H	2.31832800	-4.60779000	0.36410600
H	3.24048400	-4.14443500	-1.06514100
C	2.04364200	0.09450300	-2.17556900
C	1.38597800	-2.21214300	-1.98089400
C	3.04261700	0.56732600	1.18557400
H	4.78834600	-0.45823200	0.50602600
C	4.11685000	0.90166600	-1.04656900
H	0.40019500	-3.23286400	-0.35565400
H	0.85551900	-4.27747900	-1.70109200
H	1.04296800	0.35356300	-2.53668200
H	2.63374900	-0.23317000	-3.05271300
C	2.74394000	1.33109300	-1.58119900
H	0.43649500	-1.91850200	-2.44166600
H	2.08668500	-2.46135900	-2.80179100
N	1.77768300	1.17662800	0.71781400
H	3.71189600	1.31286500	1.64779300
H	2.78432300	-0.14889000	1.97419500
H	4.71645200	0.45233800	-1.84881600
H	4.68802700	1.75350500	-0.66119800
C	1.93502400	2.05368900	-0.48101800
H	2.86489700	2.04380900	-2.40765200
C	1.05621400	1.88411300	1.80352100
C	2.51702600	3.44984900	-0.15561400
H	0.91573300	2.21675500	-0.85509600
H	1.01952500	1.21653900	2.67069200
C	1.63483100	3.25381800	2.18760300
H	0.02307900	2.02259000	1.45777500
H	2.51055400	4.05039400	-1.07475100
H	3.56586700	3.37387200	0.15910600
C	1.71735100	4.15326500	0.94908200
H	0.99714400	3.70381800	2.95899600
H	2.63254200	3.13980300	2.63365800
H	0.70113300	4.36586500	0.58705700
H	2.17458800	5.11963400	1.19527200
Li	0.33838400	-0.38696700	0.17282200

Structure: TS33

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               23-Aug-2010
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1580.7363578\MP2=-1584.8424
927\RMSD=8.262e-09\PG=C01 [X(C26H48Li1N3S1)]\\@
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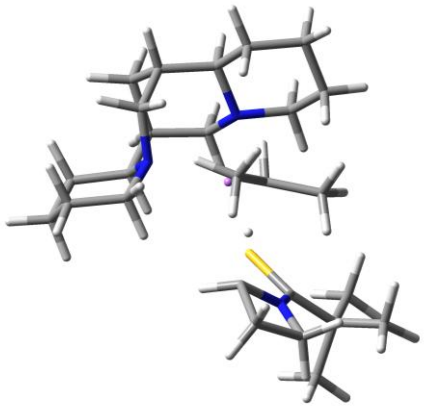

```
0 1
 H                  4.55998000   -0.14712200    1.91138200
 C                  4.21416500   -1.06448200    1.42837400
 N                  3.10297500   -0.81872300    0.46970300
 C                  3.24850000   -1.92611600    2.27215000
 C                  2.11476100   -1.45323100    1.32914600
 H                  1.54742500   -2.22362600    0.79573500
 H                  1.20218000   -0.50037900    1.79111000
 H                  5.06542300   -1.58364500    0.97888700
 H                  3.48647400   -2.99559400    2.22790300
 H                  3.15949000   -1.63105800    3.32150300
 C                  2.96704300   -0.26508200   -0.72062500
 S                  1.39684000   -0.32838900   -1.45207400
 C                  4.19690400    0.28618500   -1.47996700
 C                  3.76778800    1.17560400   -2.66458300
 H                  4.66432600    1.53084700   -3.18729900
 H                  3.20101500    2.04730200   -2.32195500
 H                  3.14194000    0.63084500   -3.37350400
 C                  5.10968000    1.14628500   -0.57278100
 H                  5.86579700    1.64506700   -1.19012900
 H                  5.64739600    0.56118500    0.17583800
 H                  4.53563300    1.92299600   -0.05480700
 C                  4.99398900   -0.91645900   -2.04537400
```

H	5.86536500	-0.56067600	-2.60903400
H	4.36777800	-1.50824600	-2.72120500
H	5.35661800	-1.58032900	-1.25321800
C	0.46926400	0.58466100	2.51861900
H	-0.36941500	1.20881400	2.15728300
C	0.00736900	-0.10558800	3.80517100
H	-0.95010100	-0.62990300	3.67669900
H	-0.12336700	0.58680600	4.65629300
H	0.73633100	-0.86295700	4.13183400
C	1.64662000	1.52539300	2.79729000
H	1.91753300	2.12243600	1.91541200
H	2.54539900	0.95363800	3.07468500
H	1.46382500	2.23097200	3.62719200
H	-2.20438800	2.04487400	1.92663000
C	-2.72369500	2.67388300	1.19448100
C	-2.92791100	1.90604200	-0.11730200
H	-3.71047500	2.90613900	1.61633200
C	-1.92327200	3.96344000	0.96581600
N	-1.63021800	1.59759100	-0.77391600
H	-3.49841200	2.58131100	-0.79018000
C	-3.79704000	0.63519500	0.02677100
C	-0.61526400	3.65421500	0.22668200
H	-1.71902000	4.46165400	1.92100300
H	-2.52545600	4.66175600	0.36603100
C	-1.85620600	0.90715000	-2.06928200
C	-0.87761800	2.84449900	-1.04360200
C	-3.19780800	-0.51606900	0.86223100
H	-4.72097600	0.94317900	0.53480900
C	-4.11866100	0.11195700	-1.37782500
H	0.05964600	3.09609900	0.88562600
H	-0.09680300	4.58163600	-0.04704200
H	-0.87727400	0.63370200	-2.47475600
H	-2.31595200	1.61798700	-2.78283100
C	-2.77931200	-0.32352800	-1.98708000
H	0.06481700	2.56001400	-1.52350200
H	-1.44260500	3.46753300	-1.76466500
N	-2.01771400	-1.16118700	0.24156600
H	-4.00998900	-1.24142100	1.03914100
H	-2.88442400	-0.15618600	1.84905100
H	-4.57612400	0.90252100	-1.98633800
H	-4.83743700	-0.71369900	-1.33790800
C	-2.19157100	-1.51641200	-1.19942500
H	-2.92614800	-0.66651500	-3.01982000
C	-1.55188700	-2.33027700	1.02734200
C	-3.00880400	-2.81026300	-1.43241000
H	-1.17568800	-1.70792500	-1.57313400
H	-1.48896700	-2.02419800	2.07576000
C	-2.39348600	-3.60402000	0.86703500
H	-0.52945600	-2.54972500	0.69819700
H	-2.98424100	-3.04429900	-2.50480400
H	-4.06374600	-2.65541300	-1.17227300
C	-2.46862200	-3.99007200	-0.61402100
H	-1.93710800	-4.40637400	1.46044700
H	-3.40567700	-3.45543200	1.26800200
H	-1.46281800	-4.25580600	-0.97031700
H	-3.09990900	-4.87535700	-0.75949300
Li	-0.29423700	0.14985200	0.34205300

Structure: TS34

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               23-Aug-2010
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1580.7366963\MP2=-
1584.8443064\RMSD=8.541e-09\PG=C01 [X(C26H48Li1N3S1)]\\@
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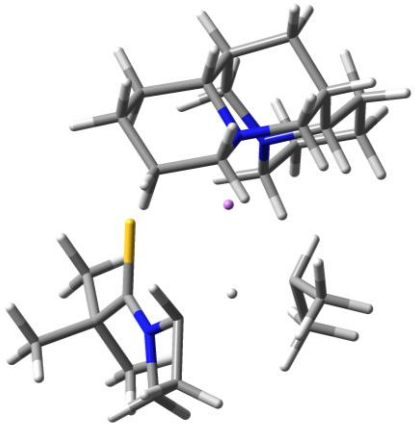

```
0 1
 H                  4.42798600    0.32258800    2.03308200
 C                  4.31102400   -0.59011200    1.44330800
 N                  3.18392100   -0.50172300    0.47573600
 C                  3.56252200   -1.73803600    2.15604800
 C                  2.35827600   -1.43010600    1.23262500
 H                  1.97345100   -2.24653400    0.61264900
 H                  1.25334200   -0.76472400    1.77557000
 H                  5.26481200   -0.84612500    0.97362500
 H                  4.03908200   -2.71363200    2.00249100
 H                  3.40137600   -1.59248800    3.22785700
 C                  2.94116800    0.13462500   -0.65619800
 S                  1.44028100   -0.20496900   -1.45306100
 C                  4.02128000    1.03690500   -1.29964000
 C                  3.42054400    1.91578000   -2.41553500
 H                  4.21768100    2.52609900   -2.85753000
 H                  2.65083400    2.58811900   -2.02295500
 H                  2.96357300    1.31343800   -3.20275700
 C                  4.67442900    1.99103400   -0.27056400
 H                  5.30168900    2.71879700   -0.79834100
 H                  5.31931200    1.47699200    0.44497300
 H                  3.91561600    2.54850200    0.29045700
 C                  5.10058900    0.12604900   -1.93712300
```

H	5.86965100	0.73688300	-2.42606700
H	4.65269200	-0.52833300	-2.69215900
H	5.59986200	-0.50597800	-1.19491800
C	0.28831300	-0.01111400	2.62738500
H	-0.68858100	0.42389100	2.34786600
C	0.04464300	-1.00329100	3.76854900
H	-0.70924200	-1.76072600	3.50944200
H	-0.29123200	-0.52684300	4.70689900
H	0.96489200	-1.55452200	4.01288700
C	1.18636900	1.14223000	3.08792500
H	1.27493600	1.92776800	2.32439200
H	2.20834600	0.78609700	3.28938800
H	0.84148700	1.62819600	4.01786300
H	-0.71591100	-1.59988200	-2.32336200
C	-1.59050000	-2.25511100	-2.25364700
C	-2.59427600	-1.70314700	-1.23482200
H	-2.07073100	-2.26468400	-3.24089900
C	-1.13463800	-3.66597500	-1.86315800
N	-2.01435100	-1.67271500	0.13678700
H	-3.45141900	-2.40960500	-1.22395600
C	-3.19569500	-0.33279700	-1.61812100
C	-0.58594400	-3.65126100	-0.43282000
H	-0.37255900	-4.02926800	-2.56236100
H	-1.98630900	-4.35954500	-1.92849400
C	-3.01557700	-1.18082600	1.11885900
C	-1.59188700	-3.03518300	0.54132600
C	-2.22413700	0.86794900	-1.62318800
H	-3.57377700	-0.43427800	-2.64425400
C	-4.35467400	-0.03936000	-0.65886000
H	0.34424900	-3.07259900	-0.41530900
H	-0.34537200	-4.66639200	-0.09276400
H	-2.50915500	-1.06997100	2.08377400
H	-3.80055100	-1.94900200	1.25364400
C	-3.72278500	0.13417600	0.72838300
H	-1.15949400	-2.96572100	1.54543400
H	-2.48161900	-3.69077500	0.61387700
N	-1.73177200	1.24345400	-0.27529900
H	-2.75146000	1.70600400	-2.10943600
H	-1.34194400	0.65433700	-2.23611200
H	-5.06881400	-0.87288800	-0.65397600
H	-4.91067200	0.85287300	-0.96607000
C	-2.80830600	1.37811100	0.74501500
H	-4.50262400	0.29883500	1.48394100
C	-0.87346200	2.45296200	-0.31149900
C	-3.60904300	2.69845400	0.64016700
H	-2.29219300	1.40660100	1.71524900
H	-0.13599400	2.30962900	-1.10696900
C	-1.62974200	3.78089800	-0.46591800
H	-0.31776600	2.47916500	0.63619900
H	-4.31233500	2.74768900	1.48205900
H	-4.21564600	2.71488900	-0.27384600
C	-2.68160700	3.92113200	0.64083900
H	-0.90776300	4.60639800	-0.42691400
H	-2.11406400	3.83677700	-1.45044900
H	-2.17568300	3.99815300	1.61449000
H	-3.26416400	4.84214900	0.51517800
Li	-0.30271800	-0.29795500	0.36300000

Structure: TS35

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1619.7867192\MP2=-
1624.0339453\RMSD=9.985e-09\PG=C01 [X(C27H50Li1N3S1)]\\@
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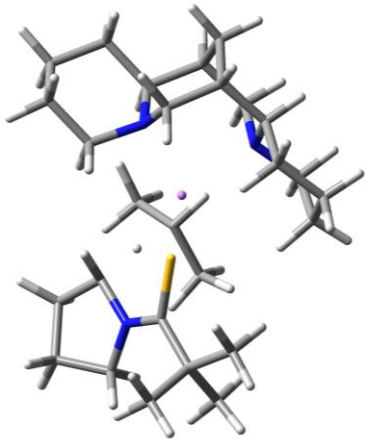

```
0 1
 C                  4.17952700   -2.21960300   -0.45048800
 C                  3.15982000   -1.22655600    0.15915900
 N                  2.11132800   -0.77329600   -0.79962700
 C                  1.49102900   -1.92399600   -1.50204400
 C                  2.48075800   -2.88565900   -2.17351100
 C                  3.48707500   -3.40235500   -1.13955000
 H                  2.61904800   -1.77219700    0.94586400
 H                  4.82016000   -1.71130300   -1.18209500
 H                  4.84118000   -2.57340300    0.35112700
 H                  0.91810700   -2.48582000   -0.75261000
 H                  0.76676500   -1.52269400   -2.21725800
 H                  1.91986300   -3.71404700   -2.62420200
 H                  3.01169900   -2.38408300   -2.99414100
 H                  2.95782700   -4.00791700   -0.38927500
 H                  4.23103000   -4.05940700   -1.60668400
 C                  2.55892700    0.27751300   -1.74504500
 H                  1.66676400    0.63312000   -2.27212300
 H                  3.23634400   -0.13099600   -2.51372900
 C                  3.86541600   -0.01672600    0.81307100
 C                  3.29929400    1.44987200   -1.06754900
 C                  4.47803600    0.89150800   -0.26139200
 H                  5.17765300    0.34840500   -0.90615300
```

H	5.04499200	1.70641900	0.20703800
H	3.66890100	2.09549500	-1.87551400
C	2.95767200	0.84132800	1.71427600
H	3.60398100	1.56727100	2.24381900
H	2.48421400	0.21914600	2.48199600
N	1.88547900	1.57110200	0.99547500
C	2.45542600	2.35119400	-0.13754400
H	3.16914800	3.09013700	0.28545000
C	1.21241900	2.47805500	1.95363200
H	1.95797500	3.16566700	2.39975000
H	0.81239800	1.86496100	2.76897300
C	1.37003500	3.15609300	-0.86192900
H	0.64125700	2.48532800	-1.32821300
H	1.84725200	3.73208500	-1.66581800
C	0.09693700	3.29233400	1.29745100
H	-0.69588000	2.61668200	0.95362600
H	-0.34319100	3.95836200	2.05031100
C	0.63307400	4.09219100	0.10440900
H	-0.18534100	4.60473800	-0.41448800
H	1.32191700	4.87150000	0.46352800
H	4.65295500	-0.42006600	1.46344500
Li	0.41273600	-0.02606000	0.31459100
C	-0.29398100	-1.09896200	2.26103700
H	0.50870200	-0.34403900	2.35341000
C	0.25914300	-2.41814300	2.81016400
H	0.55346300	-2.36544400	3.87417400
C	-1.46798200	-0.59691800	3.10831300
H	-2.34741600	-1.24749400	2.98794600
H	-1.25268800	-0.56872800	4.19162900
H	-1.78219400	0.41361700	2.81272600
S	-1.31005600	0.62650100	-1.33813600
C	-2.85928100	0.19908000	-0.68458200
H	-4.31573800	-1.37698900	1.48421400
N	-3.00773900	-1.01179500	-0.14198000
C	-4.25419500	-1.60365200	0.41269700
C	-1.91595700	-1.96204200	0.02779500
C	-2.56406000	-3.28640500	0.45696500
H	-2.41097400	-3.47916800	1.52726300
H	-2.14404000	-4.14481700	-0.07973300
H	-0.48652900	-3.22149000	2.73728000
H	-1.36230400	-2.02400400	-0.91190500
H	-1.01575400	-1.47001500	0.99826100
H	1.14106300	-2.76585100	2.25294200
H	-5.13715400	-1.20517000	-0.07661400
C	-4.06427500	-3.10127100	0.18057700
H	-4.29893100	-3.34172600	-0.86370300
H	-4.71925800	-3.70035100	0.82332800
C	-4.05234600	1.19061600	-0.83230400
C	-3.56619900	2.58117400	-1.30321100
H	-4.43654900	3.24321200	-1.39245700
H	-3.06442900	2.53252100	-2.27083100
H	-2.86742500	3.02525800	-0.58858300
C	-5.03393400	0.68568300	-1.92281000
H	-5.84642900	1.41035500	-2.05702500
H	-5.49221700	-0.28049000	-1.69467100
H	-4.50993400	0.58487700	-2.87928600
C	-4.77571100	1.44115600	0.51718700

```
 H                 -5.50355400    2.25143600    0.39191100
 H                 -4.05681900    1.75565400    1.28246200
 H                 -5.32068500    0.58048700    0.90531500
```

Structure: TS36

```
****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
                22-Feb-2011
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1619.790129\MP2=-
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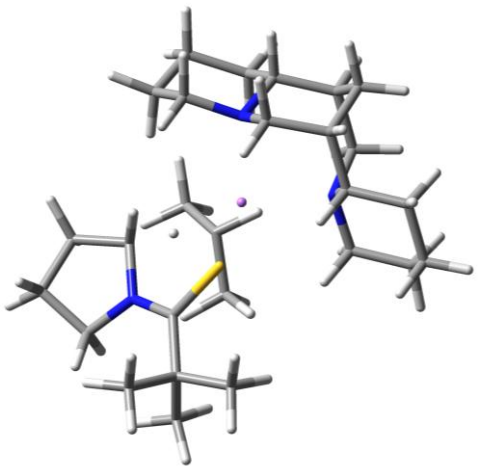

```
0 1
 C                 -2.96454600   -3.26082900   -0.32999500
 C                 -2.24881100   -1.91273700   -0.58360400
 N                 -1.99733600   -1.12449400    0.65986200
 C                 -1.33887900   -1.95892700    1.69457800
 C                 -2.04737700   -3.28482800    2.00828800
 C                 -2.22928300   -4.10048800    0.72303000
 H                 -1.25374600   -2.15569500   -0.97857700
 H                 -3.99784000   -3.09939100    0.00306300
 H                 -3.02499000   -3.80555800   -1.28136500
 H                 -0.32757600   -2.17659300    1.32720200
 H                 -1.23023300   -1.34740400    2.59646700
 H                 -1.45084800   -3.83951400    2.74367100
 H                 -3.02489900   -3.10002100    2.47499700
 H                 -1.24232100   -4.39116000    0.33554200
 H                 -2.77775200   -5.02951400    0.92240600
 C                 -3.19360600   -0.42637500    1.17879100
 H                 -2.86156400    0.21837200    2.00082100
 H                 -3.92559800   -1.12964700    1.61183200
 C                 -2.99032100   -1.05326700   -1.63218700
```

C	-3.93579700	0.39610700	0.10581900
C	-4.31312900	-0.52954900	-1.05675400
H	-4.96036200	-1.34512800	-0.71644100
H	-4.87223400	0.02299900	-1.82296700
H	-4.84321600	0.79115700	0.58234000
C	-2.18152500	0.14518500	-2.16414100
H	-2.74391200	0.57307000	-3.01579300
H	-1.21020100	-0.18356400	-2.54928100
N	-1.92540000	1.21019100	-1.16158700
C	-3.17948300	1.61534300	-0.46943400
H	-3.86086500	2.05443900	-1.22827500
C	-1.33075600	2.37439600	-1.85738100
H	-2.02535300	2.73059000	-2.64308000
H	-0.42137000	2.02975500	-2.36151400
C	-2.89478000	2.71697100	0.55879200
H	-2.22405100	2.33788600	1.33791200
H	-3.83797600	2.99154300	1.04911100
C	-1.01356000	3.52243200	-0.89771000
H	-0.22727000	3.20817500	-0.20245200
H	-0.61493600	4.36606400	-1.47515600
C	-2.25945200	3.94265900	-0.10950300
H	-2.00275900	4.69913500	0.64152600
H	-2.98909600	4.40544800	-0.79009500
H	-3.18356700	-1.70158700	-2.49713200
Li	-0.41651500	0.33421600	0.17101200
C	0.42490700	1.27286700	2.12493500
H	-0.59382000	0.84113200	2.20821700
C	0.37259800	2.66543000	2.76396400
H	0.05775900	2.64971000	3.82350700
C	1.37588300	0.36624200	2.91503500
H	2.41532000	0.71495000	2.81382800
H	1.16615300	0.34127300	4.00007400
H	1.35563600	-0.67098300	2.55582400
S	1.17691400	-1.03521500	-1.15800600
C	2.77276500	-0.69924700	-0.57835800
H	4.45455700	1.02207100	1.30109500
N	3.07574800	0.55575500	-0.23880700
C	4.39480500	1.07581000	0.20678900
C	2.10627100	1.64875300	-0.22671800
C	2.91851000	2.93566200	-0.01735400
H	2.81177500	3.31089100	1.00917100
H	2.59257100	3.74285300	-0.68277900
H	1.36308600	3.14111800	2.74938900
H	1.55733000	1.62952600	-1.17299600
H	1.18485300	1.44683700	0.81380300
H	-0.30972200	3.34882100	2.24030300
H	5.21300900	0.49989100	-0.21392000
C	4.37859300	2.52718200	-0.26681900
H	4.61425300	2.56502900	-1.33754000
H	5.11544100	3.13885500	0.26594900
C	3.82914800	-1.84428500	-0.53961500
C	3.16095400	-3.22289700	-0.75192800
H	3.93826800	-3.99634300	-0.71876900
H	2.64866700	-3.28518000	-1.71324900
H	2.42703700	-3.43757000	0.02996900
C	4.84412000	-1.67134900	-1.69983800
H	5.56331900	-2.49947100	-1.69115800

```
 H                    5.41594300   -0.74053300   -1.65202800
 H                    4.32005100   -1.68829100   -2.66137700
 C                    4.54312900   -1.93642200    0.83502000
 H                    5.13360600   -2.85921800    0.87260500
 H                    3.80807500   -1.97812600    1.64667700
 H                    5.22693700   -1.11351300    1.04521100
```

Structure: TS37

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1619.7870731\MP2=-1624.0
33523\RMSD=9.351e-09\PG=C01 [X(C27H50Li1N3S1)]\\@
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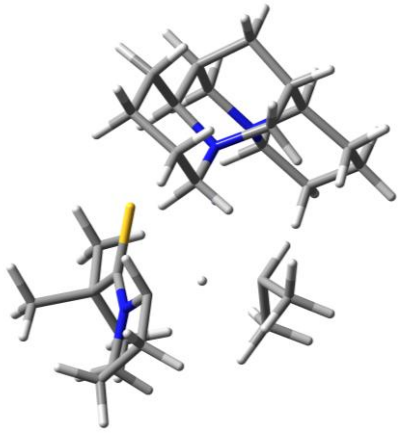

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0 1
 C                    3.07556200    2.58664900   -1.85072200
 C                    2.30389400    1.32008800   -1.40774900
 N                    2.09650800    1.21997700    0.06953900
 C                    1.57163000    2.49114200    0.62693100
 C                    2.36914800    3.74923800    0.25541100
 C                    2.46743000    3.86856000   -1.26895200
 H                    1.29372500    1.39467000   -1.83609700
 H                    4.12771000    2.52566400   -1.54476000
 H                    3.07238600    2.62419100   -2.94795300
 H                    0.54816900    2.60927600    0.25314100
 H                    1.50081200    2.37457300    1.71223600
 H                    1.86840000    4.62478800    0.68772900
 H                    3.37572900    3.71613100    0.69466300
 H                    1.46157200    4.02217700   -1.68631900
 H                    3.06646900    4.74061200   -1.55899600
```

C	3.27447000	0.73520200	0.82748600
H	2.93737200	0.54181200	1.85222100
H	4.05828500	1.50837700	0.89711500
C	2.96862000	0.03661900	-1.95734000
C	3.93591700	-0.52117300	0.22545000
C	4.29640600	-0.23239700	-1.23620500
H	4.98465300	0.61672700	-1.31191600
H	4.80515800	-1.09501100	-1.68538300
H	4.84821600	-0.70516100	0.80888300
C	2.10006100	-1.23061600	-1.86202100
H	2.62246200	-2.03199900	-2.41937900
H	1.13381100	-1.07840100	-2.35219600
N	1.83612600	-1.69236000	-0.47662100
C	3.11050700	-1.82745500	0.27779500
H	3.73197800	-2.59113400	-0.23663000
C	1.13770100	-2.99757900	-0.55215300
H	1.75766400	-3.71315500	-1.12742700
H	0.21032000	-2.83878800	-1.11210300
C	2.86353400	-2.35402500	1.69720100
H	2.28661600	-1.62487300	2.27752600
H	3.83338100	-2.46667200	2.19938400
C	0.84113100	-3.58274500	0.82886700
H	0.10957300	-2.95145500	1.34613300
H	0.37533500	-4.56786500	0.70065100
C	2.11891000	-3.69558000	1.66905100
H	1.88321300	-4.02343800	2.68855300
H	2.77499000	-4.46329400	1.23322100
H	3.14702500	0.20670800	-3.02737100
Li	0.40756100	-0.12568900	0.31196900
C	-0.46953000	-0.21225400	2.46205100
H	0.34569800	-0.92035600	2.22050000
C	-1.68111500	-1.05956000	2.86633300
H	-1.52862400	-1.63118700	3.79940100
C	0.01126400	0.64425600	3.63834500
H	-0.70288200	1.44790900	3.86753400
H	0.14097000	0.07049400	4.57449200
H	0.97488400	1.13265500	3.43533800
S	-1.24077500	-0.16944500	-1.53322500
C	-2.83208500	-0.10306400	-0.84780300
N	-3.05931700	0.75369200	0.15013300
C	-2.01533100	1.55960800	0.77543100
H	-1.13510900	0.71143800	1.47565800
H	-1.44721700	2.05321500	-0.01850700
C	-4.35915500	1.03709500	0.81509900
C	-4.21005900	2.48536100	1.27730200
H	-4.92566600	2.73658700	2.06846400
C	-2.73775600	2.53703900	1.71266700
H	-2.31978200	3.54848800	1.65545800
H	-4.38676300	3.15976700	0.43031900
H	-2.56544300	-0.42699800	3.03680200
H	-5.19337900	0.89132400	0.13565000
H	-4.48211500	0.36387800	1.67200500
H	-1.95774400	-1.77949400	2.08389900
H	-2.65410000	2.21989300	2.76111600
C	-3.96931900	-0.96206200	-1.47689500
C	-3.39449100	-2.03072400	-2.43607100
H	-2.72461400	-2.71955800	-1.91345500

```
 H                 -2.83450900   -1.58429200   -3.25902000
 H                 -4.22832700   -2.60931200   -2.85263000
 C                 -4.77329800   -1.75464000   -0.41195200
 H                 -4.09647000   -2.33335700    0.22679700
 H                 -5.43838000   -2.46306100   -0.91931500
 H                 -5.39889700   -1.13889000    0.23443300
 C                 -4.89603100   -0.06089300   -2.33507700
 H                 -5.40045100    0.72297400   -1.76319800
 H                 -5.67228500   -0.67152000   -2.81225800
 H                 -4.31541800    0.42741500   -3.12494400
```

Structure: TS38

```
 ****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1619.7863808\MP2=-
1624.0345581\RMSD=9.981e-09\PG=C01 [X(C27H50Li1N3S1)]\\@
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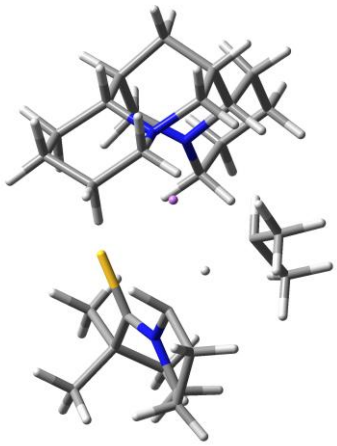

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0 1
 C                 -3.72949900    2.54533000    1.06472100
 C                 -2.92262200    1.22806000    0.98445800
 N                 -1.87278300    1.23006000   -0.07202100
 C                 -1.01969500    2.43984000    0.02050900
 C                 -1.78297600    3.77202500    0.05582500
 C                 -2.80665900    3.76388500    1.19796500
 H                 -2.38192500    1.13866700    1.93787200
 H                 -4.35710600    2.67304300    0.17400600
 H                 -4.41314600    2.48462000    1.92195000
 H                 -0.43404200    2.34953000    0.94571200
 H                 -0.30851200    2.40120900   -0.80969200
```

H	-1.06266700	4.59047700	0.18057100
H	-2.29332900	3.94846800	-0.90085000
H	-2.27610900	3.71938200	2.16046300
H	-3.39536800	4.68952200	1.20547400
C	-2.39854100	1.02105200	-1.44284200
H	-1.53033100	0.89528600	-2.09850100
H	-2.94457400	1.90756300	-1.80763400
C	-3.83123600	-0.01070100	0.83568300
C	-3.36112100	-0.18081500	-1.56282500
C	-4.49736300	-0.01682500	-0.54652300
H	-5.06287300	0.90369700	-0.72663200
H	-5.20922200	-0.84853600	-0.62647200
H	-3.76399500	-0.15891400	-2.58423400
C	-3.10583400	-1.35606000	1.04516300
H	-3.88167900	-2.14271800	1.10655800
H	-2.57405500	-1.35680500	2.00294500
N	-2.12852400	-1.71695600	-0.01448500
C	-2.74424600	-1.58358600	-1.36477000
H	-3.59768300	-2.29259700	-1.41651400
C	-1.69025000	-3.11542200	0.20782100
H	-2.57345200	-3.78399300	0.20726400
H	-1.24487800	-3.17178500	1.20693200
C	-1.76622600	-2.00012100	-2.46989100
H	-0.90655000	-1.32273900	-2.49582000
H	-2.28049300	-1.90778300	-3.43558600
C	-0.69242000	-3.58742900	-0.85040400
H	0.22753500	-2.99675200	-0.77573700
H	-0.42744300	-4.63198500	-0.64406000
C	-1.27284900	-3.43709900	-2.26063600
H	-0.52059400	-3.69497100	-3.01506500
H	-2.11134200	-4.13718300	-2.39211500
H	-4.59243900	0.05314200	1.62476800
Li	-0.40440100	-0.36175400	0.29522700
C	0.31991000	-0.28822200	2.52125100
H	-0.65344500	0.18700000	2.29666100
C	1.21378700	0.79782700	3.12938000
H	0.85861800	1.16568900	4.10860700
C	0.05791200	-1.41153700	3.53013600
H	0.97978600	-1.96435100	3.75678600
H	-0.33467000	-1.05244900	4.49874600
H	-0.66025900	-2.15353900	3.15281800
S	1.23993200	-0.04191200	-1.53792000
C	2.75062900	0.36265900	-0.78890400
N	3.16629600	-0.38185500	0.23954300
C	2.37356100	-1.44196200	0.84975200
H	1.26306800	-0.88033600	1.52294600
H	1.96543700	-2.07311400	0.05639500
C	4.45695500	-0.26561200	0.96894500
C	4.72482100	-1.69501800	1.43550000
H	5.44731900	-1.72741000	2.25890400
C	3.31668800	-2.18427100	1.80802400
H	3.21667900	-3.27238400	1.72375200
H	5.13117500	-2.28092500	0.60186900
H	2.23437400	0.42182400	3.29523200
H	5.24124900	0.12764500	0.33034600
H	4.32896200	0.40880700	1.82446900
H	1.30661300	1.67111000	2.46891100

```
 H                     3.10708800   -1.92922500    2.85540600
 C                     3.62602100    1.50105100   -1.39461800
 C                     2.82635400    2.32908900   -2.42760400
 H                     1.95752600    2.81207300   -1.97106700
 H                     2.46731000    1.71502200   -3.25478900
 H                     3.48173600    3.11149700   -2.83011300
 C                     4.82647700    0.89441000   -2.16863300
 H                     4.46319300    0.22653300   -2.95701300
 H                     5.51442300    0.32085400   -1.54137300
 H                     5.40676200    1.69486900   -2.64389500
 C                     4.09377400    2.51969200   -0.32209400
 H                     3.23507000    2.90327800    0.24089600
 H                     4.57300700    3.37197800   -0.81810900
 H                     4.81250300    2.12337200    0.39545100
```

Structure: TS39

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
Version=EM64L-G09RevA.01\State=1-A\HF=-1332.9905746\MP2=-
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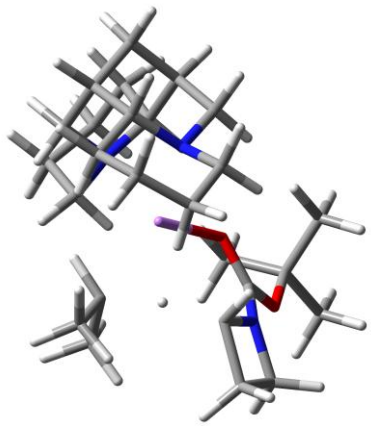

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0 1
 H                     4.13137600    3.11760000   -0.89124100
 C                     3.49657800    2.88710900   -0.02650800
 N                     2.42743600    1.93572100   -0.34615400
 C                     2.40428100    3.94205300    0.30318700
 C                     1.31197700    2.89076800   -0.08144900
 H                     0.83101000    3.14696000   -1.03820500
 H                     0.39859600    2.30870000    0.92345100
 H                     4.13704100    2.56233400    0.80147700
```

H	2.39657800	4.24661400	1.35503400
H	2.45066900	4.84534600	-0.31506400
C	2.41966600	0.61567000	-0.42048300
O	1.36759200	-0.07400600	-0.49193400
C	-0.28910300	1.89969800	2.11963500
H	-1.06323100	1.11210700	2.21861100
C	0.86084100	1.56203700	3.07777200
H	1.28646700	0.56687100	2.88567700
H	0.57762600	1.59254400	4.14496100
H	1.68366900	2.28230500	2.95619900
C	-0.93849000	3.23099200	2.51053700
H	-1.86861400	3.41849900	1.95598400
H	-0.26452400	4.07118900	2.28160500
H	-1.18376600	3.30686000	3.58394900
H	-3.05677500	1.66321800	0.92520100
C	-3.68798300	1.64003100	0.02922300
C	-3.30223600	0.44521200	-0.85104200
H	-4.72490200	1.50797800	0.36534800
C	-3.53339300	2.95805700	-0.73882900
N	-1.89563700	0.57237000	-1.31780400
H	-3.96341500	0.47890400	-1.74298400
C	-3.56905300	-0.92746400	-0.19561100
C	-2.11304600	3.06619700	-1.30326600
H	-3.75234400	3.81104400	-0.08560700
H	-4.26554600	2.98974400	-1.55934000
C	-1.49490300	-0.57814100	-2.16434900
C	-1.73562600	1.81773300	-2.10338500
C	-2.75474100	-1.24624700	1.07396000
H	-4.62713300	-0.92982400	0.09924100
C	-3.31264800	-2.02029900	-1.23937100
H	-1.39970700	3.19820200	-0.48387400
H	-2.01809800	3.94318100	-1.95606000
H	-0.42038600	-0.48409500	-2.35424400
H	-2.01190300	-0.51532900	-3.14099900
C	-1.81337800	-1.96049000	-1.56019400
H	-0.69055700	1.87582700	-2.42753600
H	-2.35823200	1.75996000	-3.01797300
N	-1.30628600	-1.40086600	0.81977800
H	-3.19296700	-2.15511600	1.52126900
H	-2.86841500	-0.44887100	1.81710200
H	-3.90576000	-1.83513400	-2.14433900
H	-3.60869900	-3.00493600	-0.86121900
C	-0.97856800	-2.31815000	-0.30984800
H	-1.56186200	-2.69897800	-2.33335100
C	-0.56218100	-1.77298800	2.04525300
C	-1.09782900	-3.81805100	0.05402200
H	0.07560200	-2.12190300	-0.54046900
H	-0.88107900	-1.09967600	2.84745700
C	-0.70049200	-3.24311900	2.46887600
H	0.49748800	-1.56075900	1.85464700
H	-0.74921700	-4.41323500	-0.80050700
H	-2.14659600	-4.09558500	0.21854600
C	-0.29202700	-4.16461100	1.31325400
H	-0.07297400	-3.41935800	3.35164600
H	-1.73380900	-3.46076400	2.77182100
H	0.78087400	-4.03654300	1.10968900
H	-0.43753200	-5.21835100	1.58171500

Li	-0.35109100	0.51793800	0.25971100
O	3.67968600	0.10405600	-0.42641800
C	3.98028700	-1.29034200	-0.74329600
C	5.51241800	-1.30252600	-0.77102400
H	5.91631800	-0.99113100	0.19766200
H	5.88891400	-0.61674300	-1.53671800
H	5.88012700	-2.30990300	-0.99373100
C	3.41693500	-1.66094500	-2.12024300
H	2.32609600	-1.63010600	-2.11927700
H	3.74186600	-2.67068600	-2.39605400
H	3.78756100	-0.96479800	-2.88078700
C	3.45997900	-2.21001700	0.36623000
H	2.37029400	-2.19207600	0.40590400
H	3.85177500	-1.89033200	1.33794200
H	3.79095500	-3.23954200	0.18607000

Structure: TS40

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               22-Feb-2011
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 --------------
 # mp2/6-31g(d)
 --------------
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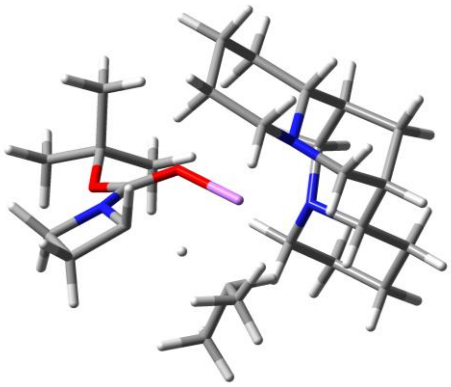

0 1

H	4.44532900	-0.53180000	2.11307900
C	4.15967200	-1.31660900	1.40366800
N	2.93316500	-1.01103500	0.65807900
C	3.44795000	-2.56631700	1.99000500
C	2.17671100	-2.19830800	1.15828100
H	2.02552600	-2.90540000	0.32882900
H	0.87809200	-1.76515900	1.72539000
H	5.01319400	-1.52210800	0.74566500
H	3.93459600	-3.51606300	1.74050100

H	3.31836300	-2.52491300	3.07677600
C	2.51812600	0.11108800	0.09623300
O	1.35496200	0.28635800	-0.35786400
C	-0.24756900	-1.48023000	2.53697000
H	-1.16792400	-0.92892700	2.26874900
C	-0.65239700	-2.90556300	2.92301600
H	-1.27857800	-3.38181700	2.15370600
H	-1.20556900	-2.97357400	3.87544500
H	0.24259900	-3.53882500	3.03066900
C	0.40215700	-0.75630300	3.72236900
H	0.61825900	0.29848200	3.49729400
H	1.36496500	-1.22426600	3.97391300
H	-0.20476700	-0.77424200	4.64441000
H	0.24057700	-0.14416000	-2.44008600
C	-0.49234000	-0.69441500	-3.03988200
C	-1.81821000	-0.80039100	-2.27613700
H	-0.66741600	-0.12444900	-3.96205900
C	0.05693300	-2.08920000	-3.36321500
N	-1.64206800	-1.55717300	-1.00664000
H	-2.51284900	-1.37536500	-2.92504400
C	-2.51436800	0.55639200	-2.02840900
C	0.18617500	-2.90169200	-2.07119400
H	1.02746300	-2.01425200	-3.86845400
H	-0.62497200	-2.60033500	-4.05899400
C	-2.92891500	-1.68376600	-0.27702600
C	-1.12784300	-2.91857000	-1.28802000
C	-1.78457600	1.53934400	-1.08693500
H	-2.58758400	1.05270300	-3.00548600
C	-3.91671700	0.27728800	-1.47513500
H	0.97541800	-2.46927300	-1.44824000
H	0.47844400	-3.93731000	-2.28558400
H	-2.71482000	-2.13650700	0.69750800
H	-3.58895700	-2.38591300	-0.82134400
C	-3.71020700	-0.36657600	-0.09776100
H	-0.99140900	-3.42841200	-0.32814200
H	-1.88724800	-3.48909700	-1.85795400
N	-1.73287100	1.08527200	0.32216400
H	-2.28885100	2.51615600	-1.18341600
H	-0.74905500	1.68336200	-1.41189500
H	-4.46252300	-0.40512500	-2.13940600
H	-4.50851500	1.19668100	-1.40728200
C	-3.04390200	0.63737100	0.86633100
H	-4.67824700	-0.64087200	0.34232800
C	-1.09817900	2.08295000	1.21552400
C	-3.98843200	1.79948000	1.25385800
H	-2.80858800	0.10544000	1.79893300
H	-0.16672300	2.40689600	0.74368900
C	-1.98561300	3.28118100	1.58463800
H	-0.82218800	1.55684300	2.13906400
H	-4.88666100	1.37787600	1.72410100
H	-4.32819000	2.34070300	0.36204500
C	-3.30016400	2.79036300	2.20282700
H	-1.43984400	3.92479600	2.28616600
H	-2.19573600	3.89376900	0.69702900
H	-3.08620800	2.29271800	3.16004700
H	-3.96745000	3.63163500	2.42705400
Li	-0.24615500	-0.53241000	0.38240700

```
 O                  3.49849500    1.05766400    0.06912300
 C                  3.52901700    2.14317800   -0.90968100
 C                  4.90742400    2.76857000   -0.67035400
 H                  5.06437900    3.61388900   -1.34887600
 H                  5.69895400    2.03199100   -0.84067600
 H                  4.99032900    3.12970000    0.35985000
 C                  2.42443100    3.16630400   -0.62437900
 H                  2.56386000    4.05196700   -1.25541800
 H                  2.46442100    3.48380600    0.42325300
 H                  1.44036200    2.74222700   -0.82575900
 C                  3.43323800    1.57649200   -2.33065200
 H                  3.56048400    2.38134000   -3.06341900
 H                  2.46312000    1.10440200   -2.50094500
 H                  4.22096100    0.83401700   -2.49915500
```

Structure: TS41

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
                7-Dec-2009
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=8
 Will use up to    8 processors via shared memory.
 ----------------------
 # m062x/6-311+g(2d,2p)
 ----------------------
Version=EM64L-G09RevA.01\State=1-A\HF=-3132.0057784\RMSD=2.914e-
09\Dipole=-1.5580966,0.3731594,-0.6532162
\Quadrupole=5.4606156,1.571722,-7.0323376,-1.854392,-
13.4977922,6.3872335\PG=C01 [X(C35H64B1F3Fe1Li1N3)]\\@
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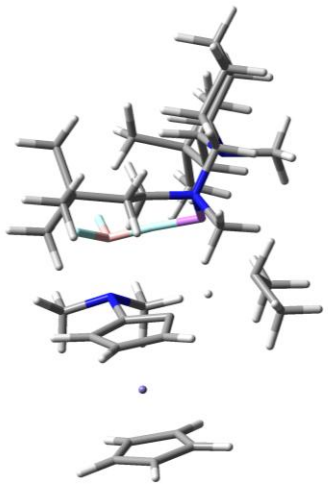

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0 1
 C                  5.54045400   -0.49817800   -1.98089500
 C                  5.27388100   -1.59426600   -1.13983100
 C                  5.79104600   -1.29306600    0.14939600
 C                  6.37598900   -0.01096800    0.09293600
```

C	6.20117100	0.49436300	-1.21772700
H	5.35028800	-0.45518700	-3.04204600
H	4.87204400	-2.54451400	-1.45204800
H	5.87203500	-1.98456500	0.97229200
H	6.95043100	0.45664600	0.87747100
H	6.64090900	1.39847200	-1.60646500
Fe	4.22691700	0.15163800	-0.34382800
C	3.03824800	1.08043300	1.20361100
C	3.18565300	1.98064400	0.14462200
C	2.61136400	1.38248600	-1.01613400
C	2.37437700	-0.07708100	0.66946200
N	1.79391700	-1.15977400	1.52583400
C	2.49284900	-1.26322800	2.85692300
C	1.88724600	-2.50327400	0.84893600
C	2.01345400	0.13028500	-0.70175700
H	3.28828500	1.27429800	2.23266200
H	3.59314000	2.97724800	0.21978800
H	2.50469800	1.89511000	-1.95711600
H	2.05957700	-2.09768300	3.40399100
H	2.33284300	-0.34758200	3.41826600
H	3.55799600	-1.42961900	2.71075800
H	2.92969200	-2.80496800	0.77603700
H	1.45856100	-2.42988100	-0.14349100
H	1.33167500	-3.22478300	1.44474400
F	-0.41967700	-0.68682300	0.58191000
Li	-0.95446300	-0.32739000	-0.90556200
B	0.15230000	-0.77832500	1.84157200
F	0.15881900	0.41443000	2.45952300
F	-0.34874900	-1.81661700	2.53356300
C	0.54282800	-2.59614400	-2.61964400
C	1.19406400	-0.46428300	-3.75256900
C	0.35870100	-1.05942300	-2.59090100
H	0.30920800	-3.02719700	-3.59371200
H	-0.08697100	-3.09809600	-1.89052400
H	1.57261500	-2.86783000	-2.39740100
H	0.94245400	-0.90761700	-4.71595100
H	2.25600800	-0.63217900	-3.59026900
H	1.04925000	0.60790700	-3.84191000
H	-0.67894900	-0.89268700	-2.91400100
H	1.15233400	-0.48344300	-1.51264300
N	-1.57013200	1.60757800	-1.11212500
C	-3.04216000	1.51336000	-1.44038600
C	-1.24524900	2.26025000	0.21332500
C	-0.84064200	2.26742700	-2.23842200
C	-3.69757100	0.30531300	-0.70457800
H	-3.08287700	1.30842100	-2.50960600
C	-3.84715400	2.81882700	-1.18009900
H	-2.01738500	1.95911400	0.91505200
H	-0.31755300	1.81287300	0.55421700
C	-1.05340200	3.80254800	0.23770600
H	-0.97895300	1.68028900	-3.14022600
H	-1.19270000	3.28349900	-2.42111000
H	0.21852800	2.29345800	-2.00447000
N	-2.91945800	-0.97214000	-0.95808700
H	-3.61719400	0.48731100	0.36673400
C	-5.20901100	0.19754000	-1.06580300
H	-3.41057200	3.63151300	-1.75334400

H	-3.78704700	3.08261800	-0.12897200
C	-5.33343900	2.66850100	-1.55739600
H	-0.16534000	4.04895100	-0.33751200
H	-1.88924900	4.30703100	-0.23383800
C	-0.87280200	4.40097900	1.66937900
C	-3.23028500	-1.55386500	-2.30580100
C	-3.27979400	-1.97245000	0.11411700
H	-5.31837700	-0.02754800	-2.12220000
H	-5.66272700	-0.61630500	-0.50815400
C	-5.96542400	1.50652500	-0.77115800
H	-5.42835800	2.48142200	-2.62514000
H	-5.85480100	3.59795700	-1.33926300
C	-0.59454600	5.91951800	1.50442800
C	-2.15851600	4.22585800	2.51945700
C	0.32713600	3.74936600	2.40403500
H	-2.49019700	-2.30650100	-2.55130600
H	-4.21951200	-2.01295000	-2.32905200
H	-3.17972500	-0.77811600	-3.06239900
H	-4.33897300	-2.22212300	0.03122600
H	-3.12517000	-1.47785400	1.06941100
C	-2.43923700	-3.26728200	0.06969700
H	-7.01037800	1.38842300	-1.04943800
H	-5.93154100	1.72394400	0.29453200
H	-0.46731200	6.39057600	2.47408800
H	0.30949700	6.08305400	0.92602900
H	-1.41863500	6.40901900	0.99433300
H	-2.36134500	3.18002200	2.72327100
H	-2.04566700	4.73354500	3.47219400
H	-3.01827600	4.65107200	2.01052100
H	1.23069700	3.83568200	1.80794300
H	0.49739600	4.24984500	3.35201200
H	0.14803600	2.69797700	2.60324400
H	-2.51610200	-3.72154700	-0.91327000
H	-1.39761400	-3.00368400	0.22587200
C	-2.84445400	-4.34186000	1.12891100
C	-4.24130800	-4.93637900	0.80909500
C	-2.84478300	-3.74867300	2.56174900
C	-1.79446500	-5.48250800	1.05658500
H	-5.01992900	-4.18491300	0.88540500
H	-4.26260200	-5.35063400	-0.19431700
H	-4.47716200	-5.73203700	1.50889700
H	-2.94013200	-4.54393400	3.29414900
H	-1.92217200	-3.20802600	2.75147100
H	-3.67666500	-3.06682600	2.70212700
H	-1.75084800	-5.90232700	0.05622300
H	-0.80759200	-5.11064400	1.31323300
H	-2.04867700	-6.27861500	1.74942900

Structure: TS42

```
 ****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
                4-Dec-2009
 ****************************************
 %nosave
 %mem=10GB
 %nprocshared=8
```

```
 Will use up to    8 processors via shared memory.
 ----------------------
 # m062x/6-311+g(2d,2p)
 ----------------------
Version=EM64L-G09RevA.01\State=1-A\HF=-3132.0044383\RMSD=3.828e-
09\Dipole=1.294849,1.2797493,0.3254845\Quadrupole=5.9850431,-
6.8396008,0.8545578,-5.5900897,1.6376604,-3.9933553\PG=C01
[X(C35H64B1F3Fe1Li1N3)]\\@
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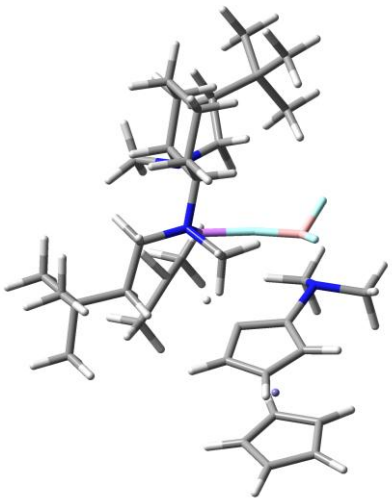

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0 1
 H                 -5.62811200    0.38603200   -2.25109400
 C                 -5.70324400   -0.32093300   -1.43953100
 C                 -5.22109700   -1.64282500   -1.45086800
 H                 -6.98151700    0.75666500    0.02777000
 H                 -4.74043600   -2.13084500   -2.28318000
 C                 -5.63695700   -2.27109000   -0.24564100
 H                 -5.54878500   -3.32155000   -0.02055900
 C                 -6.37590500   -1.33002200    0.50096500
 H                 -6.92003200   -1.53187500    1.41052000
 C                 -6.39831600   -0.11424200   -0.22381000
 Fe                -4.31830700   -0.59795100    0.24291500
 H                 -3.26353300   -1.13835500    2.95919000
 C                 -3.09761500   -0.62504100    2.02736700
 C                 -3.46130600    0.69546600    1.74742300
 H                 -3.97404500    1.36197200    2.42415400
 C                 -2.93919400    1.02623600    0.46122200
 H                 -2.97978000    2.01585500    0.03818100
 C                 -2.35602900   -1.09753600    0.89092600
 F                  0.42518300   -1.00862700    0.43671300
 C                 -0.26761000   -0.79335500   -3.14043600
 H                  0.02919700   -0.53113700   -4.15663700
 H                  0.51269800   -1.43319700   -2.73648900
 H                 -1.16550700   -1.40104300   -3.22710900
 C                 -1.63356700    1.28888800   -2.95122000
 H                 -1.38141200    1.54220700   -3.98095600
 H                 -2.57301400    0.74175700   -2.97585200
 H                 -1.82083100    2.21953300   -2.42498300
 Li                 0.74933400    0.33809000   -0.41334600
```

B	0.05422800	-1.98819500	1.34079900
F	-0.00078100	-1.48788500	2.58896100
F	0.77307100	-3.11133700	1.17078300
N	-1.55792100	-2.36522300	0.89710400
C	-2.08256500	-3.36076100	1.89900400
H	-1.49452300	-4.27188600	1.81207100
H	-1.96769300	-2.95639300	2.90025100
H	-3.13047300	-3.57698400	1.70178600
C	-1.56733600	-3.02323300	-0.45926000
H	-2.56672000	-3.39088100	-0.68086200
H	-1.27173800	-2.29498000	-1.20489800
H	-0.85981600	-3.84999300	-0.44307000
N	2.77843100	0.16878800	-0.91356700
N	1.22052600	1.75128900	0.96920900
C	2.61658900	1.28879400	1.34294900
H	2.48137100	0.31539800	1.81408600
C	3.48816000	1.07901700	0.06587300
H	3.56668600	2.04081200	-0.43814000
C	4.93375800	0.63816900	0.43434600
H	5.53514800	0.60083800	-0.46933900
H	4.91969000	-0.35721500	0.86618700
C	3.33520200	2.22090300	2.36267700
H	3.43862000	3.21732900	1.94468800
H	2.73732500	2.30243200	3.26557500
C	4.74083500	1.70242200	2.71870800
H	5.20715400	2.38286900	3.42781900
H	4.66894200	0.72745500	3.19652800
C	5.59659100	1.59472300	1.44455600
H	5.71389400	2.58098400	0.99996400
H	6.59007800	1.22427800	1.68757400
C	3.03181800	-1.31043900	-0.72670200
H	3.08103700	-1.49521800	0.34202400
H	2.14402000	-1.81512600	-1.09203700
C	3.08359600	0.59607800	-2.31452600
H	2.72419900	1.60993800	-2.46343400
H	4.15301600	0.56796100	-2.53012500
C	0.30704100	1.58433200	2.14838600
H	-0.71758600	1.74172800	1.82965800
H	0.38852900	0.57172500	2.53216600
C	1.20644000	3.19583500	0.53580000
H	1.97959700	3.32071600	-0.21534200
H	1.45572100	3.83133200	1.38643500
C	-0.52881700	0.45249900	-2.25794500
H	0.37075100	1.07543200	-2.36836400
C	-2.16692900	-0.04638400	-0.06552900
H	-1.31511600	0.11989100	-1.07237600
H	0.54119100	2.29531700	2.94172000
C	-0.15399400	3.64103600	-0.04461800
H	-0.48932400	2.89433000	-0.75813500
H	-0.88556300	3.67793500	0.75725900
C	-0.13776400	5.03536700	-0.74769600
C	0.71817000	4.99854300	-2.04039000
H	1.76579000	4.82437700	-1.81924000
H	0.37237500	4.21262300	-2.70473100
H	0.64244100	5.94587800	-2.56508600
C	0.40256100	6.13690700	0.20174800
H	0.29721200	7.11311200	-0.26116000

H	-0.14991700	6.14445500	1.13647000
H	1.45331300	5.98633200	0.42587200
C	-1.60059800	5.38386200	-1.13124700
H	-2.01310800	4.63012100	-1.79429500
H	-2.22625300	5.43862400	-0.24571700
H	-1.64254300	6.34325900	-1.63747100
H	2.56398800	-0.05608800	-3.00966400
C	4.25202500	-1.94505000	-1.45064900
H	4.06764000	-1.92148300	-2.52102300
H	5.15630400	-1.37488400	-1.27042900
C	4.52616300	-3.42879000	-1.04453100
C	5.63442400	-3.97188500	-1.98627100
H	5.88322400	-4.99692000	-1.72990300
H	5.30384600	-3.95074600	-3.02013100
H	6.53614300	-3.37262300	-1.90446700
C	5.03246500	-3.52305800	0.41861300
H	4.27561600	-3.19474800	1.12293700
H	5.28603700	-4.55079800	0.65871800
H	5.92081600	-2.91465700	0.55833500
C	3.25586600	-4.30361600	-1.20723200
H	2.84442100	-4.20137000	-2.20681200
H	3.50325000	-5.34846100	-1.04818300
H	2.49128200	-4.02685900	-0.48848300

Structure: TS43

```
*****************************************
 Gaussian 09:  EM64L-G09RevA.01  8-May-2009
               14-Oct-2010
 *****************************************
 %nosave
 %mem=10GB
 %nprocshared=4
 Will use up to    4 processors via shared memory.
 ----------------------
 # m062x/6-311+g(2d,2p)
 ----------------------
Version=EM64L-G09RevA.01\State=1-A\HF=-3130.8068871\RMSD=3.179e-
09\Dipole=0.929155,0.9088956,0.7817668\Quadrupole=6.7114163,2.1319114,
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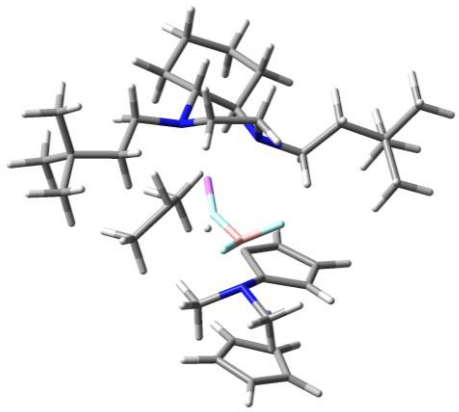

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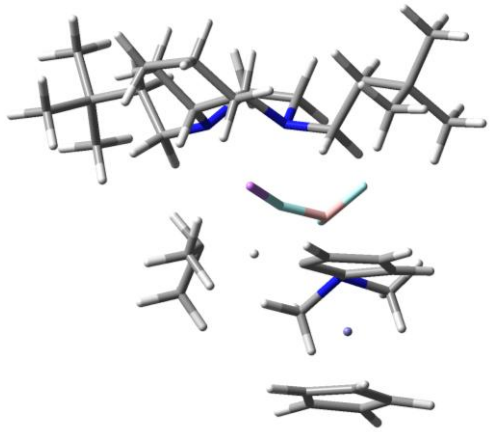

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6.Appendix

6.1 Fundamental Quantum Mechanics in Chemistry

Quantum mechanics provides useful tools for the study of reaction mechanisms. Many mathematical approaches for the calculation of the energy of molecular systems have been developed. They allow for geometry modifications which result in the minimized energies. In this vein, stationary points along a given reaction coordinate can be found thus providing insight to the reaction mechanism.

The famous equation in quantum mechanics that describes the energy of a system described by the wavefunction, Ψ, is the Schrödinger equation 1.[68]

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t) = E\Psi(x,t) \qquad \textbf{Equation (6.1)}$$

This equation is an eigenvalue problem in which the Hamiltonian operator, $\hat{H}$, extract the energy eigenvalue, E. The Hamiltonian operator is shown in equation 6.2 where V is the potential energy operator and the second order differential operator extracts the kinetic energy eigenvalue. [68]

$$\hat{H}\Psi(x,t) = \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \Psi(x,t) \qquad \textbf{Equation (6.2)}$$

When the potential energy operator is not time dependent, separation of variables can be used to explain a stationary state of the wave function, ψ which is independent of time, in the time-independent Schrödinger equation shown below. [68]

$$\hat{H}\psi = E\psi \qquad \textbf{Equation (6.3)}$$

The potential energy operator is dependent on the system being studied. Equation 6.4 represents this operator. [68]

$$V_e = \sum_{i=1}^{n-1} \sum_{j=1+i}^{n} \frac{1}{r_{ij}} - \sum_{i}^{n} \sum_{\alpha}^{N} \frac{Z_\alpha}{r_{\alpha i}} \qquad \textbf{Equation (6.4)}$$

The first term accounts for the Coulombic repulsion between each pair (i, j) of the electrons. The second term describes the Coulombic attraction between each of the electrons (i) and each of nuclei (α). To calculate the energy of a molecule, it is necessary to add the electrostatic repulsion between each pair of nuclei (α,β), V_N, as well. [ref] According to the Born-Oppenheimer approximation, kinetic energy of the nuclei can be neglected given that their motion is insignificant compared to that of electrons. [68]

$$V_N = \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \qquad \textbf{Equation (6.5)}$$

For a multi electron molecule in three dimensions, the time-independent Hamiltonian is defined as follows: [68]

$$\hat{H} = \sum_{i=1}^{n} \frac{-\hbar^2}{2m_e} \nabla^2 + \sum_{i=1}^{n-1} \sum_{j=1+i}^{n} \frac{1}{r_{ij}} - \sum_{i}^{n} \sum_{\alpha}^{N} \frac{Z_\alpha}{r_{\alpha i}} + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \qquad \textbf{Equation (6.6)}$$

The independent Schrödinger equation 6.3, along with the molecular Hamiltonian, equation 6.6, gives the energy of a molecular geometry with clear dependence on

nuclear positions. Since the wave function describing the molecule is unknown, the variational principle should be used in order to calculate the unknown wave function.

$$E \leq \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \qquad \textbf{Equation (6.7)}$$

Equation 6.7 emphasizes that the expectation value for energy of *any* normalized trial wave function, ψ, is less than or equal to the factual ground state energy of the system, E. Therefore, by describing a trial wave function and modifying it in a way that the expectation value for energy is minimized, it would be possible to obtain the true wave function and true ground state energy.

Most quantum mechanical calculations on molecular systems use the Molecular Orbital approximation. This allows a wave function to be expressed as an antisymmetric product of molecular orbitals, ϕ, as shown in equation 6.8. [68]

$$\psi = |\phi_1 \phi_2 \cdots \phi_n| \qquad \textbf{Equation (6.8)}$$

Each orbital is described as a linear combination of hydrogen-like atomic spin orbitals, and describes a stationary state for the system that is being investigated. [68]

6.2 The Hartree-Fock Method

One particle systems can be subjected to exact quantum mechanical calculations, however, electron-electron repulsion prevents analytical calculation of molecular systems. In 1928, Hartree suggested a method for the consideration of this electrostatic coupling. [68] His method employs the Molecular Orbital approximation to average the location of electrons 2, 3,..., n over all space, and then calculate the electrostatic repulsion felt by electron 1 in the presence of this average field. [68] Equation 6.9 represents the repulsion between electrons 1 and i. [68]

$$V_{1-i} = \int_{all\,space} \frac{\phi_i^* \phi_i}{r_{1i}} d\tau_i \qquad \textbf{Equation (6.9)}$$

When this operator is used in the Hamiltonian operator, an interesting challenge arises. While determining the wave function of a system via the Variational Principle requires that the Hamiltonian operator is known, the electron-electron repulsion operator contains molecular orbitals from the wave function vis-á-vis (**Equation6.9**). This gives rise to the self-consistent field (SCF) method.[68] Each iteration entails the application of the variational principle to the time independent Schrödinger equation 6.10, where φ^i is the trial function for the ith iteration, and $V\left(\varphi^{i-1}\right)$ is the potential energy operator. The dependence of $V\left(\varphi^{i-1}\right)$ on the trial function φ^{i-1} , results from the required estimation of electron-electron repulsion.

$$\left[\frac{-\hbar^2}{2m_e}\nabla^2 + V\left(\varphi^{i-1}\right)\right]\varphi^i = E\varphi^i \qquad \textbf{Equation (6.10)}$$

A first estimate is made for the trial function φ^0 and electron-electron repulsion is neglected for the first iteration.[68] The trial function φ^1 obtained from the first iteration is subsequently used to construct $V(\varphi^1)$ for the second iteration to be initiated. Iterations are conducted continuously until $\varphi^i = \varphi^{i-1}$.[68]

Pragmatically, the SCF method is applied to each Molecular Orbital independently as in the differential equation 6.11.[68]

$$\hat{F}\phi_i = \varepsilon_i \phi_i \qquad \textbf{Equation (6.11)}$$

The Fock operator $\hat{F}$ is similar to the Hamiltonian operator, but is applied to each spin orbital ϕ_i independently. The eigenvalue, ε_i, represents the orbital energy for the i^{th} molecular spin orbital.

6.3 Approximating Atomic Orbitals

In order to generate an accurate wavefunction, a trial function must have an accurate functional form. This can be achieved by constructing Molecular Orbitals using linear combination of hydrogen-like atomic orbitals.[68] For instance, the 1s orbital is shown as follows [68]:

$$1s = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} \qquad \textbf{Equation (6.12)}$$

In this mathematical representation, the charge of the nucleus is Z, a is the Bohr radius, and r is the electron's distance from the nucleus. Nevertheless, performing calculations on functions of this form are computationally demanding. To efficiently use computational resources, orbital functions are approximated by a linear

combination of gaussian functions that are noticeably easier to integrate. A gaussian function is represented as follows:

$$e^{-\zeta r^2}$$ **Equation (6.13)**

A basis set represents the number and type of gaussian functions used to describe each atomic orbital. For example, a 6-31G(d) basis set uses 6 gaussian functions to model core orbitals. The valence orbitals are expressed by three narrow gaussian functions, and one broader gaussian. [68] Since the valence orbitals are represented by two different variances of gaussian functions, this basis set is referred to as split-valence double zeta. The (d) shown in the basis set indicates that d orbitals are added to non-hydrogen atoms. [68] An effort that is done to eliminate basis functions that contribute the least to a basis set, is called contraction and lessens computational expense. Since the eliminated basis functions contribute the least to the set, error associated with the contraction is limited.

6.4 Effective Core Potentials

Owing to the fact that each electron occupies an orbital described by several basis functions, *ab initio* methods become more demanding as the number of atomic orbitals in the system increases. Accordingly, the expense of computational study of heavy atoms (i.e. transition metals) rises. The development of effective core potential (ECP) basis sets such as LANL2MB, resulted in more efficient calculation of such atoms.[63] In this basis set, only valence electrons are explicitly described for atoms Na through Bi.[63] The rationale for this description is based upon the fact that valence electrons are ,

almost entirely, responsible for the chemical behaviour of heavy atoms. Core electrons for these atoms are implicitly described by an electrostatic potential function $U_l(r)$ that contributes to the overall energy. The dependence on angular momentum quantum number l of interacting valence electron indicates that the interaction energy depends on the ability of valence electrons to penetrate the core orbitals. To compensate for the departure of core orbitals from their canonical description, valence orbitals φ_l are described by polynomial functions $\tilde{\varphi}_l$, whose order depends on the angular momentum. The new functions $\tilde{\varphi}_l$ experience the effective core potential $U_l(r)$ according to eigenvalue equation 6.14.

$$\left[\frac{-1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-\frac{Z}{r}+U_l(r)+\tilde{V}_{val}\right]\tilde{\varphi}_l(r)=\varepsilon_l\tilde{\varphi}_l(r) \qquad \textbf{Equation (6.14)}$$

The first two operators in equation 6.12 are the kinetic energy and centrifugal operators, respectively. Nuclear-electron attraction is represented by the third operator. The fourth operator, $U_l(r)$, describes electron-electron repulsion that exist between core and valence electrons and the final operator, $\tilde{V}_{val}$, describes existing interactions between the valence electrons. The ECP $U_l(r)$ is determined numerically from 6.14 by $\tilde{\varphi}_l$ being smooth, containing no nodes, and being equal to φ_l in the valence region of space.

6.5 Density Functional Theory

An obvious departure from the conventional Schrödinger equation is noted in the beginning of Density Functional Theory (DFT). The molecular properties are computed as functionals of electron density, ρ, as a substitute to computing as a functional of the wavefunction, ψ. [68] In this line, electronic energy in DFT is indicated by $E[\vec{\rho}(r)]$, representing that energy is a functional of electron density which, in turn, is a function of position. Each component of the electronic energy can also be expressed as a functional of ρ as shown in equation 6.15 where $\langle T[\vec{\rho}(r)]\rangle$ is the average kinetic energy, $\langle V_{NE}[\vec{\rho}(r)]\rangle$ is the average nuclear-electronic attraction, and $\langle V_{ee}[\vec{\rho}(r)]\rangle$ is the average electron-electron repulsion. [68]

$$E[\vec{\rho}(r)] = \langle T[\vec{\rho}(r)]\rangle + \langle V_{NE}[\vec{\rho}(r)]\rangle + \langle V_{ee}[\vec{\rho}(r)]\rangle \qquad \textbf{Equation (6.15)}$$

Among the indicated terms in equation 6.13, only V_{NE} can be explicitly described, which is represented in 6.16 where r_α is the electron's distance from nucleus α and Z_α is the charge on nucleus α. [68]

$$V_{NE} = -\sum_{\alpha} \int \frac{Z_\alpha \rho(r)}{r_\alpha} dr \qquad \textbf{Equation (6.16)}$$

The $\langle T[\vec{\rho}(r)]\rangle$ term in equation 6.16 is described by the kinetic energy of a hypothetical non-interacting electron gas, T_s, with a perturbation, ΔT_s. Likewise, the $\langle V_{ee}[\vec{\rho}(r)]\rangle$ term is treated as a function of average electron

separation, $\frac{1}{2}\iint \frac{\vec{\rho}(r_1)\vec{\rho}(r_2)}{r_{12}} d\tau_1 d\tau_2$, with a perturbation ΔV_{ee}. [68] The unknown functions, ΔV_{ee} and delta ΔT_s are brought together in a term called the exchange-correlation energy, E_{xc}. [68] The energy functional, therefore, reduces to equation 6.17.

$$E = -\sum_{\alpha} \int \frac{Z\vec{\rho}(r)}{r_\alpha} d\vec{r} + \frac{1}{2}\iint \frac{\vec{\rho}(r_1)\vec{\rho}(r_2)}{\vec{r}_{12}} d\tau_1 d\tau_2 + T_s + E_{XC} \qquad \textbf{Equation (6.17)}$$

It is noteworthy that the first three terms in 6.17 are easily evaluated functionals of ρ whereas the last one is an unknown functional which contributes insignificantly to the energy. Although the accuracy of the calculated energy depends on E_{XC}, the slight contribution of this term limits the magnitude of the error. [68]

The exchange-correlation functional must be approximated since it is not known exactly. Contained within E_{XC} are a number of different components divided into exchange and correlation terms. [68] Exchange energy accounts for interactions of same spin electrons and results from the Pauli Exclusion Principle. A kinetic correlation term describes small energetic differences in kinetic energy of electrons in the molecular system compared to a non-interacting electron gas. [68] Electrostatic interactions between electrons of opposite spin are specified by coulombic correlation energy.[68] Two distinct types of correlation functionals are local, depending on electron density only, and gradient corrected functionals which depend both on electron density and its gradient. [68] The well known B3LYP exchange-correlation functional contains a gradient corrected correlation functional, a density functional exchange term, and a Hartree-Fock

exchange term. The incorporation of HF exchange term represents the B3LYP functional as a hybrid one.

6.6 Perturbation Theory

Dependable energies of molecular systems can be calculated by using perturbation theory. Perturbation theory is based upon the principle of describing the true Hamiltonian operator, H, as a sum of two operators (**Equation 1.18**).[68]

$$H = H^0 + H' \qquad \textbf{Equation (6.18)}$$

H^0 is an approximate Hamiltonian for which the eigenfunctions and eigenvalues are known and H' represents a perturbation. Møller and Plesset [69] developed a perturbation theory that was applicable to molecular systems in which H^0 is the Hartree-Fock Hamiltonian and H' represents electron correlation. Truncating the Taylor-series expansion of Møller-Plesset energy at the second order term brings about the Møller-Plesset second order perturbation (MP2) energy. [69] The MP2 energy calculation involves the use of doubly excited stationary states that are eigenfunctions of H^0.[68]